Supporting Information

Peng, H. L., Payton, J. L., Protasiewicz, J.D. & Simpson, M. C.

"Twisting the Phenyls in Aryl Diphosphenes (Ar-P=P-Ar). Significant Impact upon Lowest Energy Excited States"

References with more than 10 authors

(**26**) 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, 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 *Gaussian03 (Rev.B.04)* **2003,** Gaussian, Inc. Pittsburgh, PA.

Table S1. Selected Geometry and Energy Results from B3LYP/6-31G+(d,p) Calculations of Ph-P=P-Ph geometry optimizations as a function of $\tau_1 = \tau_2 = \tau$ (PPCC) phenyl twist angle, and for the central Ph-P=P-Ph cores of the crystal structures of Dmp-P=P-Dmp and Mes*-P=P-Mes* diphosphenes.

τ (PPCC) /Degrees	r(P=P) /Å	r(P-C) /Å	θ(PPC) /Degrees	E(HOMO-1) /eV	E(HOMO) /eV	E(LUMO) /eV	Relative Total E[d] /eV
0	2.0563	1.8393	104.1	-6.689	-6.069	-2.933	0.0324
15	2.0572	1.8385	103.6	-6.717	-6.085	-2.917	0.0184
30	2.0577	1.8388	102.3	-6.788	-6.140	-2.877	0.0034
32.4[a]	2.0576	1.8385	102.2	-6.792	-6.146	-2.875	0.0000
45	2.0563	1.8416	101.0	-6.879	-6.224	-2.843	0.0242
60	2.0532	1.8473	100.2	-6.981	-6.307	-2.847	0.0907
75	2.0504	1.8534	99.9	-7.056	-6.363	-2.879	0.1632
90	2.0494	1.8559	99.8	-7.073	-6.384	-2.899	0.1945
62.0[b]	2.0463	1.8662	102.4	-6.859	-6.234	-2.816	0.5179
81.2/13.0[c]	1.9849	1.8403	97.5	-6.588	-6.394	-2.709	0.2378
		1.8420	109.8				

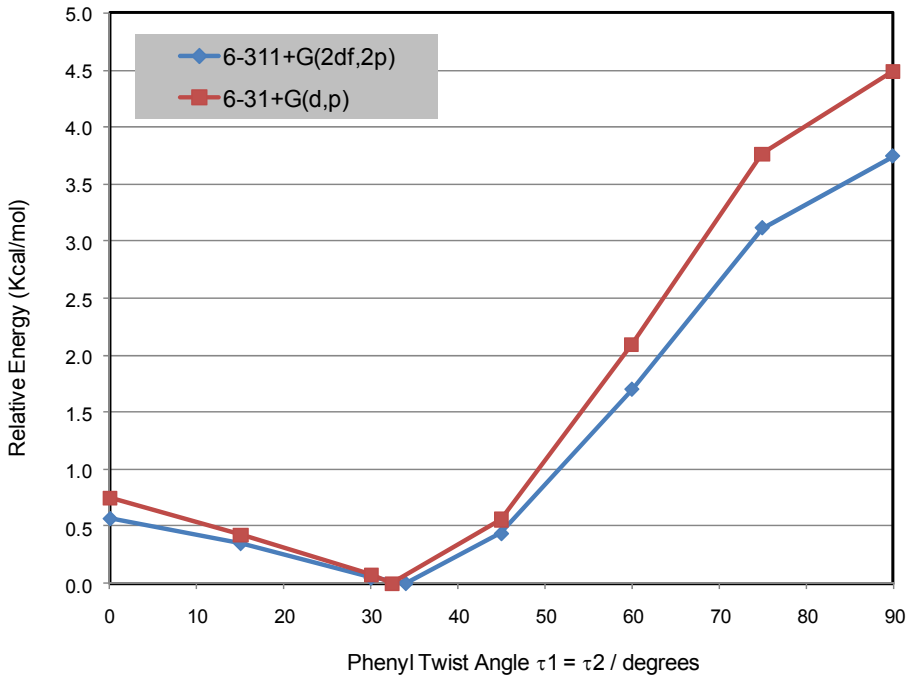
a. Minimum energy, unconstrained geometry of Ph-P=P-Ph at this level of computation.
b. Ph-P=P-Ph core crystal structure of Mes*P=PMes* (reference 24).
c. Ph-P=P-Ph core crystal structure of DmpP=PDmp (reference 25).
d. Relative to the energy of the 32.4° minimum energy structure.

Table S2. Selected Geometry and Energy Results from B3LYP/6-311G+(2df,2p) Calculations of Ph-P=P-Ph geometry optimizations as a function of $\tau_1 = \tau_2 = \tau$ (PPCC) phenyl twist angle.

τ (PPCC) /Degrees	r(P=P) /Å	r(P-C) /Å	θ(PPC) /Degrees	E(HOMO-1) /eV	E(HOMO) /eV	E(LUMO) /eV	Relative Total E[b] /eV
0	2.0436	1.8307	104.2	-6.646	-6.087	-2.886	0.0246
15	2.0443	1.8301	103.7	-6.676	-6.103	-2.869	0.0151
30	2.0447	1.8301	102.5	-6.751	-6.155	-2.824	0.0021
34.0[a]	2.0446	1.8302	102.3	-6.770	-6.167	-2.817	0.0000
45	2.0430	1.8328	101.2	-6.847	-6.234	-2.778	0.0189
60	2.0398	1.8385	100.3	-6.952	-6.311	-2.767	0.0737
75	2.0367	1.8443	100.0	-7.034	-6.363	-2.783	0.1349
90	2.0355	1.8467	99.9	-7.060	-6.379	-2.795	0.1621

a. Minimum energy, unconstrained geometry of Ph-P=P-Ph at this level of computation.
b. Relative to the energy of the 34.0° minimum energy structure.

Figure S1. A. Comparison of the ground state potential energy for Ph-P=P-Ph using B3LYP and the two basis sets 6-31+G(d,p) and 6-311+G(2df,2p). **B.** Comparison of these diagonals ($\tau_1 = \tau_2$) along the PES for Ph-P=P-Ph for both basis sets with that of a model diphosphene designed to simulate the Mes* ligand (bis-(2,6-*t*$Bu_2C_6H_2$)diphosphene) at the B3LYP/6-31+G(d,p) level.



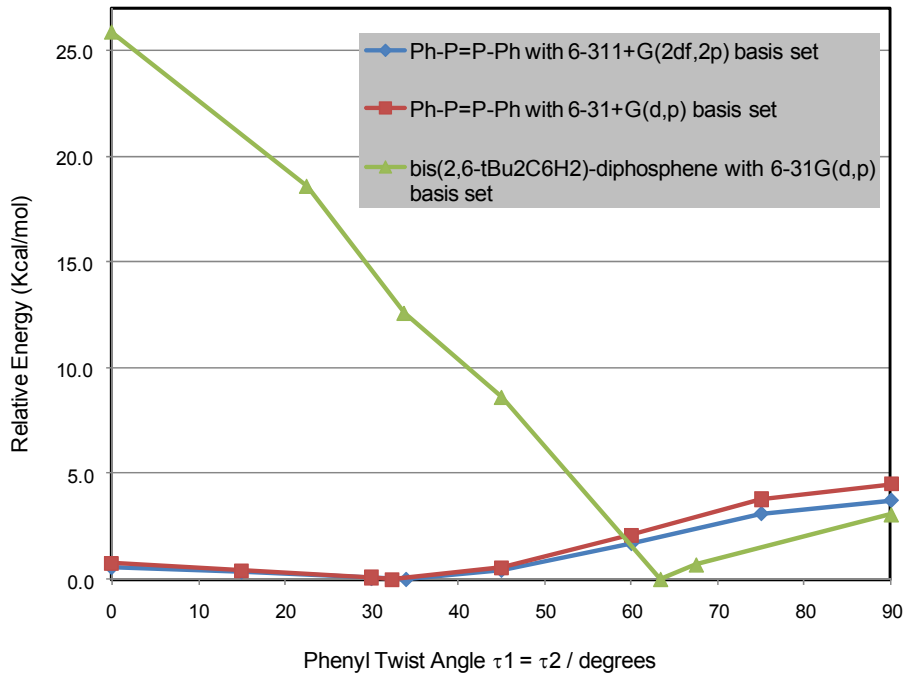


Figure S2. Comparison of the Kohn-Sham molecular orbital energies for Ph-P=P-Ph using B3LYP and the two basis sets 6-31+G(d,p) and 6-311+G(2df,2p).

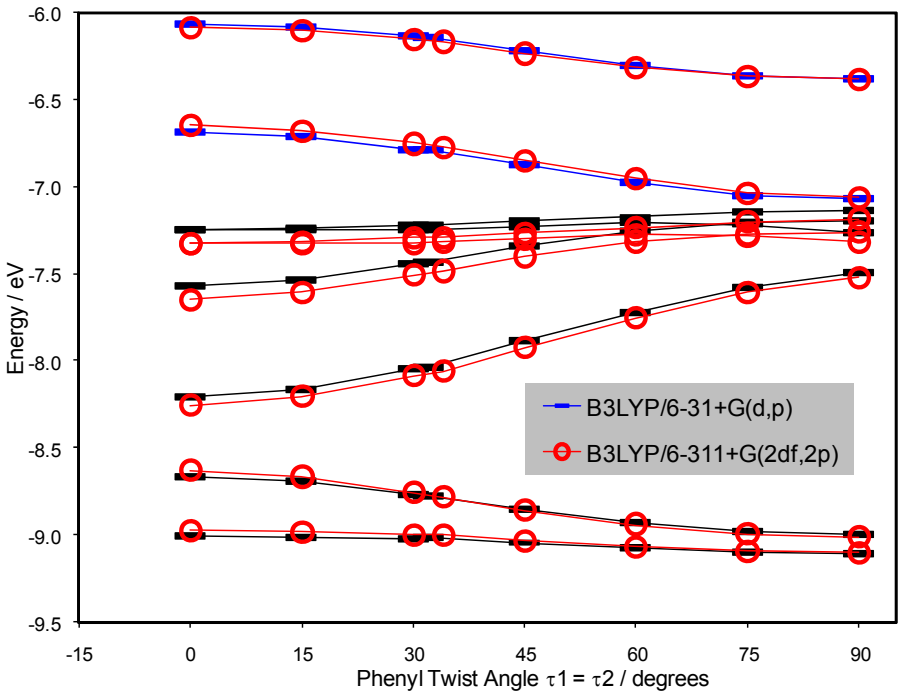
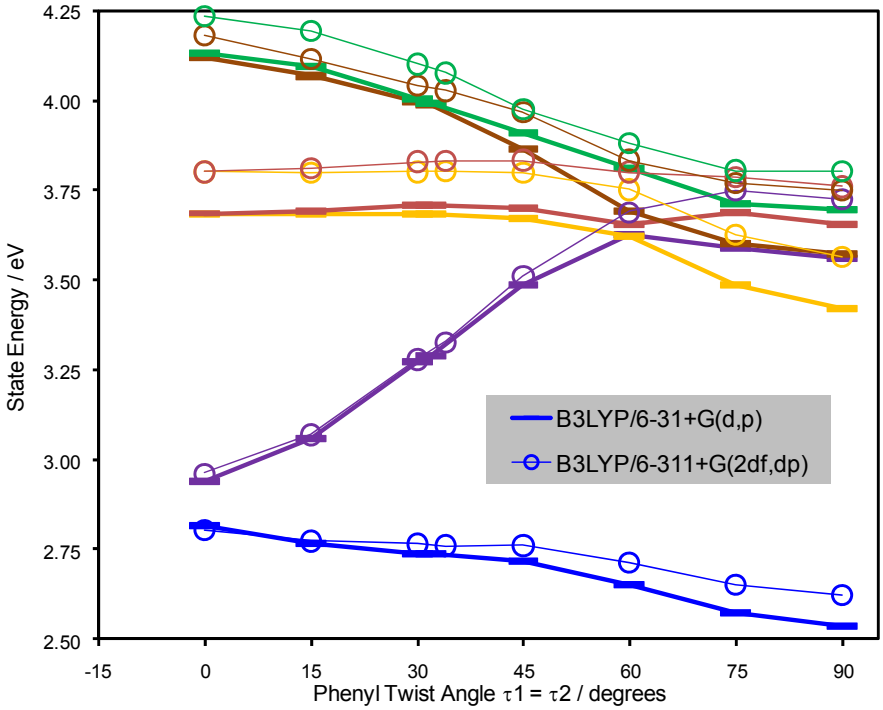



Figure S3. Comparison of the energies of the first several singlet excited states for Ph-P=P-Ph using B3LYP and the two basis sets 6-31+G(d,p) and 6-311+G(2df,2p).