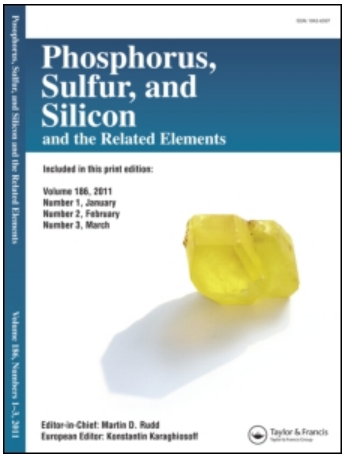

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An Ab Initio Molecular Orbital Study of Valence Bond Isomers of Silabenzene and Phosphabenzene

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AN AB INITIO MOLECULAR ORBITAL STUDY OF VALENCE BOND ISOMERS OF SILABENZENE AND PHOSPHABENZENE

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Ab initio molecular orbital calculation at HF/6-31G, HF/6-31G**, HF/6-311G**, HF/6-311++G**, RMP2-FC/6-31G*, and B3LYP/6-31G* levels of theory for geometry optimization and MP4(SDQ)/6-31G* for a single point total energy calculation are reported for silabenzene (**7**), phosphabenzene (**8**) and 16 valence bond isomers of silabenzene and phosphabenzene (**9–24**). The calculated energy difference (19.78 kcal mol^{-1}) between silabenzene and the most stable valence bond isomer of silabenzene (1-silabenzvalene, **9**) is much smaller than the difference (73.60 kcal mol^{-1}) between benzene and benzvalene (**2**). The energy difference between phosphabenzene and the most stable valence bond isomer of phosphabenzene (1-phosphabenzvalene, **17**) is calculated to be 43.29 kcal mol^{-1}.*

Keywords: Ab initio calculations; phosphabenzene; silabenzene; stereochemistry; strained molecules; valence bond isomers

The valence bond isomers of benzene have been the subject of intensive experimental and theoretical studies.[1–3] Benzene itself has long been know to be a planar regular hexagon (**1**), described as a resonance hybride of two equivalent Kekulé structures. Benzvalene (**2**) and Dewar benzene (**3**) were first prepared in the 1960s.[4–9] Triangular prismane (**4**) was synthesized in the 1970s.[10] Bicyclopropyl-2,2′-diene (**5**) was finally realized in 1989.[11] The synthetic history of these isomers implies something about their relative stabilities or energies. The sixth valence

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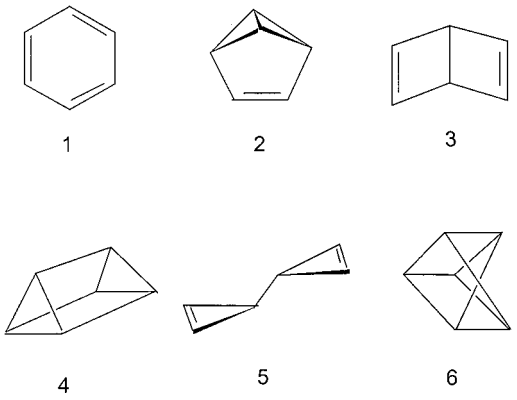
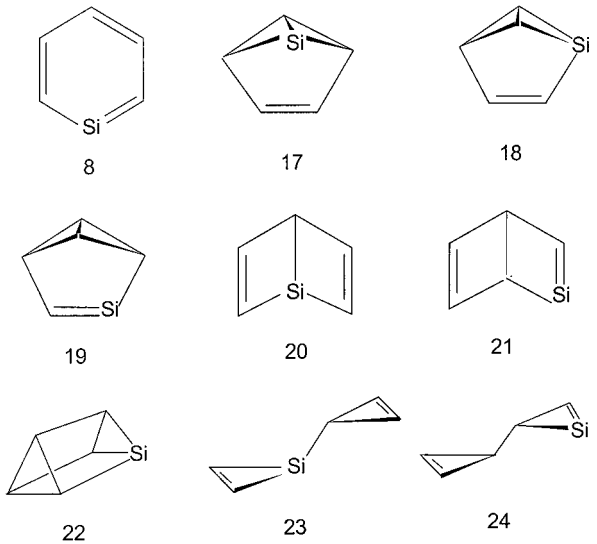
bond isomer of $(CH)_6$, benzmobiusstripane (**6**),[12] is chemically unrealistic (Scheme 1) and is not considered in this report.

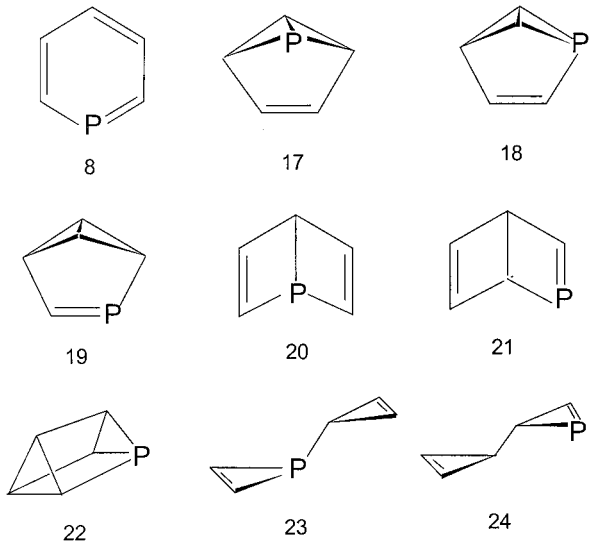


SCHEME 1

While much work has been dedicated to the study of structure and properties of $(CH)_6$ isomers **1–5**,[1–12] as well as, to the valence bond isomers of pyridine,[13,14] much less effort has been devoted to systematic study of valence bond isomers of silabenzene and phosphabenzene. The number of different positions that a silicon atom or a phosphorus atom can occupy in $(CH)_6$ isomers **1–5** is nine (see Schemes 2 and 3). This



SCHEME 2



SCHEME 3

study was undertaken to investigate the structural optimization of silabenzene (**7**) and phosphabenzene (**8**) and their valence bond isomers (**9–24**). The results from MP4(SDQ)/6-31G*//RMP2-FC/6-31G* calculations are used in the energies discussions below.

RESULTS AND DISCUSSION

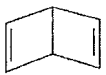
Benzene

The results of ab initio calculations for benzene and its valence bond isomers (**2–5**) are shown in Table I. All of the basis sets employed in these calculations give the same order of stabilities for compounds **1–5** (Table I). Benzvalene (**2**) and Dewar benzene (**3**) are less stable than benzene by 73.60 and 77.09 kcal mol^{-1} respectively. The calculated energy for prismane (**4**) and bicyclopropyl-2,2′-diene (**5**) are 115–122 kcal mol^{-1} higher than that for benzene. The *anti*, C_{2h}, form of (**5**) is more stable than the *syn*, C_{2v}, geometry, as indicated by all of the methods, except for the B3LYP, which gives slightly lower energy for the latter conformation (see Table I).

Silabenzene

Aromatic compounds containing silicon have attracted considerable interest, both experimentally[15–23] and theoretically,[24–26] and efforts

TABLE I Total Energies (Hartree) and Relative Energies (in Parentheses, kcal mol^{-1})[a] of Benzene (**1**) and Valence Isomers of Benzene (**2–5**)

Structure	 **1**, D_{6h}	 **2**, C_{2v}	 **3**, C_{2v}	 **4**, D_{3h}	 **5**-*anti*, C_{2h}	 **5**-*syn*, C_{2v}
HF/6-31G*//HF/6-31G*	−230.7031137	−230.570812	−230.565319	−230.503287	−230.494781	−230.491784
	(0.0)	(83.03)	(87.74)	(125.41)	(130.74)	(132.63)
ZPE	65.57189	66.25935	66.23833	66.14040	63.45549	63.40514
HF/6-31G**//HF/6-31G**	−230.713858	−230.582294	−230.576321	−230.514986	−230.506365	−230.503350
	(0.0)	(82.56)	(86.31)	(127.79)	(130.20)	(132.09)
HF/6-311G**//HF/6-311G**	−230.754097	−230.621681	−230.616962	−230.552752	−230.548586	−230.545439
	(0.0)	(83.09)	(86.05)	(126.35)	(128.96)	(130.93)
HF/6-311++G**//HF/6-311++G**	−230.756847	−230.623836	−230.619255	−230.553975	−230.550835	−230.547551
	(0.0)	(83.46)	(86.34)	(127.30)	(129.27)	(131.33)
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−231.457733	−231.338981	−231.329561	−231.270111	−231.257698	−231.256101
	(0.0)	(74.52)	(80.43)	(117.73)	(125.52)	(126.53)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−231.493431	−231.376143	−231.370581	−231.309509	−231.298511	−231.296270
	(0.0)	(73.60)	(77.09)	(115.41)	(122.31)	(123.72)
B3LYP/6-31G*//B3LYP/6-31G*	−232.248661	−232.119343	−232.114240	−232.055035	−232.044769	−232.042005

[a] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

in this area have been intensified since the first synthesis of stable silenes and disilenes.[18] Silabenzene and 1-methylsilabenzene have been identified in an argon matrix at 10 K.[15–17] 1-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-silabenzene recently was isolated in C_6D_6 by Wakita and coworkers.[27] 2,6-Bis(trimethylsilyl)-1,4-di-*tert*-butyl-1-silabenzene survives only below -100°C and is stabilized by the coordination of the solvent.[28]

Silabenzene, a 6π-electron cyclic species involving Si—C multiple bonds, long resisted attempts to demonstrate its existence conclusively by observation of any of its molecular state fingerprints. Our knowledge of these silicon compounds are derived from quantum chemical calculations and spectroscopic investigations[29–33] as the main sources of reliable information.

The valence bond isomers of silabenzene derived from benzvalene (**2**) and Dewar benzene (**3**) are expected to be more stable than those formally derived from prismane (**4**) and bicyclopropyl-2,2′-diene (**5**). The results of ab initio calculations for valence bond isomers **9–13** are given in Table II. 1-Silabenzvalene (**9**) is the most stable valence isomer of silabenzene. The 2-sila and 3-sila isomers are less stable than **9** by 20.7 and 49.2 kcal mol^{-1} respectively. The plane-symmetrical Dewar silabenzene **12** is calculated to be 28.5 kcal mol^{-1} more stable than the unsymmetrical Dewar silabenzene **13**.

The calculated energy difference between silabenzene and 1-silabenzvalene (**9**) is quite small (19.78 kcal mol^{-1}) compared to the relative energies of their C_6H_6 analogues. Although structure **9** lacks aromaticity, it contains no Si—C multiple bonds. In view of the relative instability generally associated with multiple bonds involving silicon, the small energy difference between silabenzene and **9** is understandable.

Silaprismane (**14**) is calculated to be 15.97 kcal mol^{-1} more stable than 1-silabicyclo propyl-2-2′-diene (**15**) (see Table III). Rotation around the single bond between the two three-membered rings in **15** and **16** leads, in each case to two conformations, namely *anti* and *syn*. In all cases, the *anti* rotamer is more stable than the *syn*.

Phosphabenzene

Since its discovery, phosphabenzene (phosphinine) has been the subject of a number of theoretical investigations.[24,34–36] These studies were motivated by the need for phosphorus chemists to have a good understanding of the electronic factors that render phosphabenzene so different from its nitrogen counterpart (pyridine) with regard to its chemical reactivity[37] and its coordination properties.[38] Phosphabenzene (**8**) is an ideal model for studying the ability of the —P=C double-bond system to

TABLE II Total Energies (Hartree) and Relative Energies (in Parentheses, kcal mol^{-1}) of Silabenzene (**7**) and Valence Bond Isomers of Silabenzene (**9–13**) Derived from Benzvalene (**2**) and Dewar Benzene (**3**)

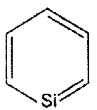
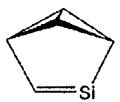
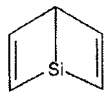
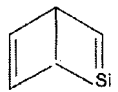
Structure	 **7**, C_{2v}	 **9**, C_s	 **10**, C_s	 **11**, C_s	 **12**, C_s	 **13**, C_l
HF/6-31G*//HF/6-31G*	−481.698968	−481.661018	−481.627170	−481.570098	−481.639792	−481.579230
	(0.0)	(23.14)	(44.47)	(79.95)	(36.37)	(74.44)
ZPE	61.48005	60.75827	60.85593	60.49554	60.65825	60.73247
HF/6-31G**//HF/6-31G**	−481.709613	−481.671697	−481.638143	−481.581236	−481.650493	−481.589993
	(0.0)	(23.12)	(44.26)	(79.64)	(36.33)	(74.37)
HF/6-311G**//HF/6-311G**	−481.764400	−481.724708	−481.692125	−481.634654	−481.705064	−481.644779
	(0.0)	(24.23)	(44.77)	(80.50)	(36.47)	(74.37)
HF/6-311++G**//HF/6-311++G**	−481.767248	−481.727246	−481.694273	−481.636895	−481.707174	−481.647438
	(0.0)	(24.43)	(45.21)	(80.88)	(36.93)	(74.48)
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−482.415632	−482.383630	−482.348374	−482.304467	−482.352742	−482.310513
	(0.0)	(19.41)	(41.62)	(68.84)	(38.70)	(65.27)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−482.454774	−482.422172	−482.389338	−482.343400	−482.397777	−482.352474
	(0.0)	(19.78)	(40.48)	(68.98)	(35.00)	(63.50)
B3LYP/6-31G*//B3LYP/6-31G*	−483.595053	−483.557796	−483.518526	−483.470766	−483.526245	−483.480143
	(0.0)	(22.71)	(47.44)	(77.08)	(41.97)	(71.41)

TABLE III Total Energies (Hartree) and Relative Energies (in Parentheses, kcal mol^{-1}) of Valence Bond Isomers of Silabenzene (**14–16**) Derived from Prismane (**4**) and Bicyclopropyl-2,2′-diene (**5**)

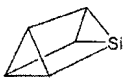
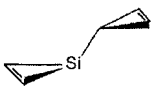
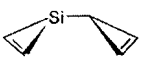
Structure	 **14**, C_s	 **15**-*anti*, C_s	 **15**-*syn*, C_s	 **16**-*anti*, C_l	 **16**-*syn*, C_l
HF/6-31G*//HF/6-31G*	−481.555696	−481.571085	−481.569747	−481.4843825	−481.479203
	(89.21)	(77.11)	(77.90)	(131.62)	(134.80)
ZPE	60.73799	58.05707	58.00780	58.16941	58.09596
HF/6-31G**//HF/6-31G**	−481.566682	−481.582345	−481.580984	−481.495662	−481.490440
	(89.00)	(76.72)	(77.53)	(131.24)	(134.43)
HF/6-311G**//HF/6-311G**	−481.619795	−481.638998	−481.637665	−481.552077	−481.546539
	(90.05)	(75.55)	(76.34)	(130.20)	(133.60)
HF/6-311++G**//HF/6-311++G**	−481.621627	−481.641030	−481.639756	−481.554670	−481.548952
	(90.69)	(76.06)	(78.98)	(130.36)	(133.88)
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−482.282553	−482.281266	−482.280483	−482.216656	−482.213137
	(82.82)	(81.17)	(81.62)	(121.82)	(123.96)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−482.323643	−482.326873	−482.325894	−482.258991	−482.255063
	(81.59)	(77.12)	(77.69)	(119.82)	(122.22)
B3LYP/6-31G*//B3LYP/6-31G*	−483.453064	−483.458918	−483.4577083	−483.3899333	−483.385412
	(88.41)	(82.28)	(83.10)	(125.68)	(128.45)

TABLE IV Total Energies (Hartree) and Relative Energies (in Parentheses, kcal mol^{-1}) of Phosphabenzene (**8**) and Valence Bond Isomers of Phosphabenzene (**17–21**) Derived from Benzvalene (**2**) and Dewar Benzene (**3**)

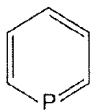
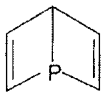
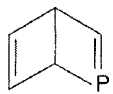
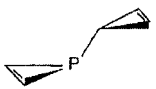
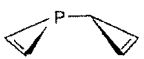
Structure	 **8**, C_{2v}	 **17**, C_s	 **18**, C_s	 **19**, C_s	 **20**, C_s	 **21**, C_l
HF/6-31G*//HF/6-31G*	−532.954812	−532.869998	−532.864223	−532.843950	−532.860634	−532.842865
	(0.0)	(52.73)	(55.93)	(68.87)	(58.06)	(69.53)
ZPE	56.80093	56.27343	55.80767	56.04331	55.66620	56.01861
HF/6-31G**//HF/6-31G**	−532.963732	−532.879205	−532.873625	−532.853343	−532.869781	−532.851848
	(0.0)	(52.55)	(55.63)	(68.57)	(57.91)	(69.49)
HF/6-311G**//HF/6-311G**	−533.017735	−532.934025	−532.927413	−532.906267	−532.924720	−532.906575
	(0.0)	(52.04)	(55.77)	(69.25)	(57.33)	(69.03)
HF/6-311++G**//HF/6-311++G**	−533.020678	−532.936793	−532.929888	−532.908391	−532.927445	−532.909142
	(0.0)	(52.15)	(56.06)	(69.76)	(57.46)	(69.27)
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−533.695405	−533.625219	−533.612155	−533.599763	−533.602299	−533.593997
	(0.0)	(43.56)	(51.33)	(59.32)	(57.38)	(62.91)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−533.731773	−533.662007	−533.650864	−533.636899	−533.645004	−533.635458
	(0.0)	(43.29)	(49.86)	(58.84)	(53.41)	(59.72)
B3LYP/6-31G*//B3LYP/6-31G*	−534.877989	−534.797395	−534.786427	−534.770260	−534.783043	−534.770070
	(0.0)	(50.09)	(56.54)	(66.90)	(58.54)	(67.00)

TABLE V Total Energies (Hartree) and Relative Energies (in Parentheses, kcal mol^{-1}) of Valence Bond Isomers of Phosphabenzene (**22–24**) Derived from Prismane (**4**) and Bicyclopropyl-2,2′-diene (**5**)

Structure	 **22**, C_s	 **23**-*anti*, C_s	 **23**-*syn*, C_s	 **24**-*anti*, C_l	 **24**-*syn*, C_l
HF/6-31G*//HF/6-31G*	−532.805310	−532.782363	−532.780072	−532.783668	−532.780654
	(93.12)	(104.38)	(105.80)	(104.64)	(106.50)
ZPE	56.05164	52.60868	52.58742	53.79346	53.75150
HF/6-31G**//HF/6-31G**	−532.814712	−532.792243	−532.789955	−532.793201	−532.790174
	(92.82)	(103.78)	(105.19)	(104.26)	(106.12)
HF/6-311G**//HF/6-311G**	−532.867404	−532.849316	−532.846971	−532.849521	−532.846187
	(93.64)	(101.85)	(103.30)	(102.80)	(104.86)
HF/6-311++G**//HF/6-311++G**	−532.869296	−532.852251	−532.849742	−532.851931	−532.848464
	(94.30)	(101.85)	(103.41)	(103.14)	(105.28)
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−533.556105	−533.522779	−533.522091	−533.538695	−533.533829
	(86.72)	(104.49)	(104.90)	(95.58)	(98.60)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−533.595967	−533.565512	−533.564117	−533.578026	−533.573325
	(84.53)	(100.50)	(101.35)	(93.73)	(96.64)
B3LYP/6-31G*//B3LYP/6-31G*	−534.732084	−534.705638	−534.703681	−534.712280	−534.709684
	(90.87)	(104.32)	(105.53)	(101.23)	(102.82)

participate in conjugative interactions.[39] Theoretical study of the gas-phase proton affinity of phosphabenzene has been reported using ab initio SCF calculations.[40]

The results of ab initio study of valence isomers of phosphabenzene (see Scheme 3) are shown in Tables IV and V. According to these calculations, 3-phosphabenzvalene (**17**) is 43.29 kcal mol^{-1} less stable than the planar 6π-electron phosphabenzene (**8**). Other valence isomers derived from benzvalene (**2**), namely 2-phospha- and 3-phospha-benzvalene, are 6.57 and 15.55 kcal mol^{-1} less stable than (**17**). The plane-symmetrical Dewar phosphabenzene (**20**) is 6.31 kcal mol^{-1} more stable than the unsymmetrical isomer **21**. As shown in Tables IV and V, structures containing P—C multiple bonds in phosphabenzenes derived from benzvalene, Dewar benzene, or bicyclopropyl-2,2′-diene are less stable than the corresponding geometries lacking such multiple bonds. The calculated energy difference (84.53 kcal mol^{-1}) between phosphaprismane (**22**) and phosphabenzene is slightly higher than that for the sila analogues **14** and **7** (see Table III and V). Rotation around the single bond between the two three-membered rings in **23** and **24** requires 0.85 and 2.91 kcal mol^{-1} respectively.

CONCLUSIONS

The ab initio calculations provide a clear picture of the energetics of valence bond isomers of silabenzene and phosphabenzene. Isomers corresponding to the sila or phospha analogues of benzvalene and Dewar benzene are more stable than the valence bond isomers derived from prismane and bicyclopropyl-2,2′-diene. The calculated energy difference between silabenzene and the most stable valence bond isomer of silabenzene (1-silabenzvalene, **9**) is much smaller than the difference between benzene and benzvalene. Similar order of stability was calculated for the phospha analogues. It would be valuable, of course, to have direct data on the valence isomers of silabenzene and phosphabenzene for comparison with the results of ab initio calculations.

CALCULATIONS

The ab initio molecular orbital calculations, were carried out using the GAUSSIAN 98 program.[41] Geometries for all structures were optimized fully by means of analytical energy gradients by Berny optimizer with no geometrical constraints.[42,43] Initial geometry optimizations were carried out at HF/6-31G* level, and zero point energies, obtained at

this level, were scaled by 0.9135. In light of the fact that correction of electron correlation is often important in conformation studies, we have made use of several methods for calculating this correction. One approach involved the density functional theory at the B3LYP/6-31G* level.[44] This makes use of a three-parameter functional that is a hybride of exact (Hartee-Fock) exchange terms, similar to those first suggested by Becke.[45] Geometry optimizations also were carried out using HF/6-31G**, HF/6-311G**, HF/6-311++G**, and RMP2-FC/6-31G* followed by a MP4(SDQ)/6-31G* calculations using the RMP2-FC/6-31G* geometry, allowing a comparison with the B3LYP/6-31G* results.

REFERENCES

[1] E. E. van Tamelen, *Acc. Chem. Res*., **5,** 186 (1972).
[2] E. E. van Tamelen, *Angew. Chem. Int. Ed. Engl*., **4,** 738 (1965).
[3] L. T. Scott and M. Jones Jr, *Chem. Rev*., **72,** 181 (1972).
[4] E. E. van Tamelen and S. P. J. Pappas, *J. Am. Chem. Soc*., **84,** 3789 (1962).
[5] E. E. van Tamelen and S. P. J. Pappas, *J. Am. Chem. Soc*., **85,** 3279 (1963).
[6] E. E. van Tamelen, S. P. Pappas, and K. L. J. Kirk, *J. Am. Chem. Soc*., **93,** 6092 (1971).
[7] K. E. Wilzabach, J. S. Ritscher, and L. J. Kaplan, *J. Am. Chem. Soc*., **89,** 1031 (1967).
[8] L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc*., **90,** 3291 (1968).
[9] H. R. Ward and Wishnok, *J. Am. Chem. Soc*., **90,** 1085 (1968).
[10] T. J. Katz and N. Acton, *J. Am. Chem. Soc*., **95,** 2738 (1973).
[11] W. E. Billups and M. H. Halrey, *Angew. Chem. Int. Ed. Engl*., **28,** 1711 (1989).
[12] A. T. Balaban, *Rev. Roum. Chem*., **11,** 1097 (1966).
[13] Y. Kobayashi and I. Kumadak, *Adv. Heterocycl. Chem*., **31,** 169 (1982).
[14] I. Yavari, Sh. Moradi, H. Kabiri-Fard, F. Nourmohammadian, and D. Tahmassebi, *J. Mol. Struct. (Theochem)*, **578,** 249 (2002).
[15] H. Bock, R. A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *J. Am. Chem. Soc*., **102,** 429 (1980).
[16] C. L. Kreil, O. L. Chapman, G. T. Burns, and T. J. Barton, *J. Am. Chem. Soc*., **102,** 841 (1980).
[17] B. Solouki, P. Rosmus, H. Bock, and G. Maier, *Angew, Chem. Int. Ed. Engl*., **19,** 51 (1980).
[18] a) G. Raabe and J. Michl, *Chem. Rev*., **85,** 419 (1985); b) A. G. Brook and M. A. Brooke, *Adv. Organomet. Chem*., **39,** 71 (1996).
[19] G. Maier, K. Schöttler, and H. P. Reisenauer, *Tetrahedron Lett*., **26,** 4079 (1985).
[20] A. Sekiguchi, G. R. Gillette, and R. West, *Organometallics*, **7,** 1226 (1988).
[21] H. Hiratsuka, M. Tanaka, T. Okutsu, M. Oba, and K. Nishiyama, *J. Chem. Soc., Chem. Commun*., 215 (1995).
[22] T. Müller, *Angew. Chem. Int. Ed. Engl*., **37,** 68 (1998).
[23] K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, P. v. R. Schleyer, and H. Jiao, *J. Am. Chem. Soc*., **121,** 11336 (1999).
[24] J. Chandrasekhar and P. v. R. Schleyer, *J. Organomet. Chem*., **289,** 51 (1985).
[25] H. Bock, *Angew. Chem. Int. Ed. Engl*., **28,** 1627 (1989).
[26] K. K. Baldridge and M. S. Gordon, *J. Am. Chem. Soc*., **120,** 4204 (1988).

[27] K. Wakita, N. Tokitoh, R. Okazaki, N. Takagi, and S. Nagase, *J. Am. Chem. Soc*., **122,** 5648 (2000).
[28] G. Markland and W. Schlosser, *Angew. Chem. Int. Ed. Engl*., **37,** 963 (1988).
[29] H. Bock and B. Solouki, *Angew. Chem. Int. Ed. Engl*., **20,** 427, 439 (1981).
[30] C. Batich, E. Heilbronner, H. Hornung, A. J. Ashe, III. D. T. Clark, D. Kilcaot, and I. Scanlan, *J. Am. Chem. Soc*., **95,** 928 (1973).
[31] H. Bock, P. Rosmus, and B. Solouki, *J. Organometallic. Chem*., **271,** 145 (1984).
[32] A. J. Ashe, III, F. Burger, M. Y, El-Sheik, E. Heilbronner, J. P. Maier, and J. F. Muller, *Helv. Chim. Acta*, **59,** 1944 (1976).
[33] J. Bastide, E. Heilbronner, J. P. Maier, and A. J. Ashe, III, *Tetrahedron Lett*., 411 (1976).
[34] L. Nyulaszi and G. Keglevich, *Heteroatom Chem*., **5,** 131 (1994).
[35] J. Waluk, H. P. Klein, A. J. Ashe, III, and J. Michl, *Organomettalics*, **8,** 2804 (1989).
[36] L. Nyulaszi and T. Veszprèmi, *J. Phys. Chem*., **100,** 6456 (1994).
[37] G. Märkl, *Multiple Bords and Low Coordination in Phosphours Chemistry*, edited by M. Regitz and O. J. Scherer (Thieme: Stuttgart, 1990), p. 220.
[38] P. Lefloch and F. Mathey, *Coord. Chem. Rev*., **179–180,** 771 (1999).
[39] L. Nyulaszi, T. Veszprèmi, and J. Rèffy, *J. Phys. Chem*., **97,** 4011 (1993).
[40] L. L. Lohr, H. B. Schlegel, and K. Morokuma, *J. Phys. Chem*., **88,** 1981 (1984).
[41] M. K. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian 98, Revision A.6, Gaussian, Inc, Pittsburgh, PA (1998).
[42] F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999).
[43] W. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1999).
[44] P. J. Stephens, F. J. Devlin, and M. J. Frisch, *J. Phys. Chem*., **98,** 11623 (1994).
[45] A. D. Becke, *J. Chem. Phys*., **98,** 5648 (1993).