Inorganic Chemistry

Article

pubs.acs.org/IC

Oxaphosphirane-Borane Complexes: Ring Strain and Migratory Insertion/Ring-Opening Reactions

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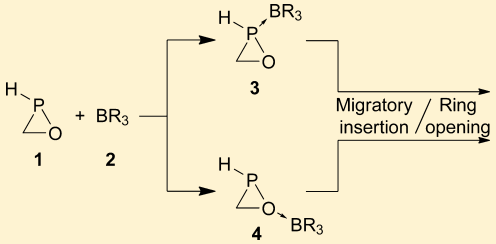
Supporting Information

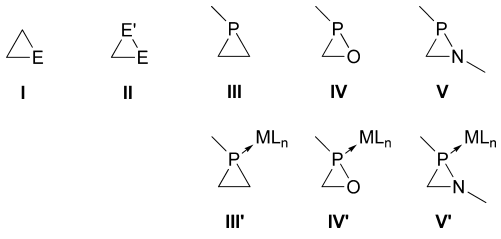
ABSTRACT: DFT-based HSAB-related parameters predict most favorable *P*- versus O-complexation of parent oxaphosphirane (**1**) with a variety of borane reagents BR_3 (**2**). In general, strong P−B bonds are formed, especially for R: H (**3a**), Cl (**3d**), and C_6F_5 (**3g**), in agreement with large dissociation energies, whereas O−B bonds are usually weaker. A remarkable increase in ring strain is observed upon *P*-complexation of phosphirane or oxaphosphiranes, especially in the case of **3g** and **3d**, whereas a moderate decrease occurs in the case of *O*-complexation for both oxirane and oxaphosphiranes. Stronger P−B bonds also correlate with larger charge transfer from the oxaphosphirane to the borane units. This in turn increases electron density at the boron center and weakens all B−R bonds, thus enabling migratory insertion/ring-opening reactions in which a substituent from the borate center shifts to a ring atom; these reactions are additionally driven by release of the high ring strain of *P*-complexes **3**.



INTRODUCTION

Three-membered heterocycles possessing one (**I**) or two (**II**) ring atoms such as nitrogen, oxygen, and/or sulfur are well-known versatile building blocks in organic synthesis (Scheme 1).[1] Among related phosphorus-containing heterocycles having four- and/or five-coordinate phosphorus centers, phosphiranes (**III**, **III′**), possessing weakly polar endocyclic bonds, are relatively well investigated.[2] Oxaphosphiranes[3−6] **IV** and azaphosphiridines[7,8] **V** received attention in the late 1970's and early 1980's because of their particular ring bonding situation having three different polar bonds. Such a pattern entails a significant synthetic obstacle, as these systems **IV**−**V** are prone to ring-opening and isomerization. Derivatives of **IV** having a three-coordinate phosphorus center are unknown, whereas there are scarce reports in the case of **V**.[7]

Scheme 1. Phosphorus-Containing Three-Membered Heterocycles III−V and *P*-Complexes of III′-V′



Therefore, several theoretical investigations on the potential energy surfaces (PES) of heterocycles **III**−**V**−**IV′**[9,10] and **V**/**V′**[11] have been performed. The ring strain of **IV** (23.5 kcal mol^{-1}) and **V** (23.7 kcal mol^{-1}) as well as those of the 2,3,3-trimethyl derivative of **V** (22.6 kcal mol^{-1}) and its *P*-oxide (38.0 kcal mol^{-1}) were reported at the CCSD(T)/def2-TZVPP level. By comparison of ring strain values for trimethyl derivatives of **IV′** (22.0 kcal mol^{-1}) and **V′** (22.9 kcal mol^{-1}) at the SCS-MP2/def2-TZVPP level, little effect upon substitution was observed. Moreover, ring bond activation studies via *N*-protonation or *N*-complexation of **V** by main group Lewis acids showed that selective endocyclic bond cleavage can be promoted. This process was easily and effectively estimated by studying the percentage variation of bond-strength related descriptors (VBSD) of the endocyclic bonds of the *N*-protonated/complexed species in relation to the free precursor.[11a]

Despite the development of an epoxide-like chemistry of κ*P*-pentacarbonylmetal(0) protected $\sigma^3\lambda^3$-oxaphosphiranes,[12] e.g., (1) reductive ring-opening reactions (ROR; M = Cr),[9] (2) acid-induced P−O selective ring expansions (M = W),[13] (3) acid-induced rearrangements (M = W),[14] (4) thermal decomposition of transient oxaphosphirane complexes possessing an exocyclic C−N double bond,[15] and (5) ring deoxygenation,[16] further use is largely hampered as no $\sigma^3\lambda^3$-oxaphosphiranes **IV** are accessible as yet. Furthermore, it has turned out that group 6 pentacarbonylmetal(0) complexes are not suited for easy decomplexation. Therefore, the search for more labile *P*-complexes **IV′** is of increasing importance, and from this point of view, *P*-borane complexes seem to constitute a highly interesting target as the strength of the P−B bond should be tunable according to the BR_3 substitution pattern. Up

Received: March 8, 2014
Published: June 5, 2014

   dx.doi.org/10.1021/ic500536h | *Inorg. Chem.* 2014, 53, 6132−6140

to now, only a theoretical study on the effect of *P*-borane complexation of azaphosphiridines **V** on ring bonds was published,[11] and a weak phosphirane-BH_3 complex experimentally reported.[17]

Based on the recently developed synthetic methodology for oxaphosphirane complexes **IV′**,[18] and its planned extension to borane analogues, the present study on the effect of oxaphosphirane ring complexation by borane Lewis acids was undertaken in a comprehensive manner, focusing on (1) the relative stabilities of *P*- versus *O*-complexes, (2) the ring strain energies, as well as (3) the migratory insertion/ring-opening reactions in which boron substituents shift to different ring atom positions to form ring-opened products. To appreciate the results presented here, the reader may also consult leading references in the field of acyclic phosphane and medium-sized phosphorus heterocycle borane complexes.[19]

COMPUTATIONAL DETAILS

Quantum chemical calculations were performed with the ORCA electronic structure program package.[20] All geometry optimizations were run with tight convergence criteria using the B3LYP[21] functional together with the RIJCOSX algorithm[22] and the Ahlrichs' segmented def2-TZVP basis set.[23] In all optimizations and energy evaluations, the latest Grimme's semiempirical atom-pairwise correction (DFT-D3 methods), accounting for the major part of the contribution of dispersion forces to the energy, was included.[24] Harmonic frequency calculations verified the nature of the computed species as minima or TS structures. From these geometries obtained at the above-mentioned level, all reported electronic data were obtained by means of single-point (SP) calculations using the same functional as well as the more polarized def2-TZVPP or def2-QZVPP[25] basis set. Thermochemical data in Table 3 were computed using the double-hybrid-meta-GGA functional PWPB95,[26] together with the def2-TZVPP basis set and the D3 correction. Complexation energies include correction for the BSSE (basis set superposition error); for species collected in Table 3 the BSSE was computed for complex **3** (or complex **8** in cases in which **3** is unstable) and added to the reference (**1**+**2**). Reported energies are corrected for the zero-point vibrational term at the optimization level. Ring strain energies (RSE) were computed as the average of the opposite values for the energy balance of the full set of three homodesmotic reactions (one per endocyclic bond) depicted in Scheme 4. Energetics for model complexes were computed using coupled-cluster theory with single–double and perturbative triple excitations (CCSD(T))[27] with atomic natural orbital (ano) basis set of pTZV quality (ano-pVTZ).[28] For comparative purposes, local correlation schemes of type LPNO (Local Pair Natural Orbital) for high level single reference methods, such as CEPA (Coupled Electron-Pair Approximation),[29] here the slightly modified NCEPA/1 version[30] implemented in ORCA, was used, as well as the spin-component scaled second-order Möller-Plesset perturbation theory (SCS-MP2) level[31] with def2-QZVPP basis set. The above-mentioned LPNO-NCEPA/1 and SCS-MP2 levels were also used for the calculation of RSEs together with the def2-TZVPP basis set. All electronic properties including HSAB (Hard/Soft Acids/Bases) and bond strength related parameters were computed at the B3LYP/def2-TZVPP level. The topological analysis of the electronic charge density, $\rho(\mathbf{r})$, within Bader's Atoms-In-Molecules (AIM) methodology[32] was conducted using the AIM2000 software[33] and the wave functions generated with the Gaussian09 software package.[34] Figure 1 was drawn with AIMAll.[35] Electric charges were obtained from the natural bond orbital (NBO) population analysis.[36]

RESULTS AND DISCUSSION

HSAB Analysis of B–O and B–P Bond Formation. The HSAB principle[37] is a fundamental concept of the modern theory of acids and bases and indicates that hard acids prefer binding to hard bases (often forming bonds with substantial ionic character) while soft acids prefer binding to soft bases (often forming bonds with substantial covalent character). Parent oxaphosphirane (**1**) can react with boranes (**2**) at either the P or the O nucleophilic centers, affording the corresponding P- or O-complexes **3** or **4**, respectively (Scheme 2). A first inspection of oxaphosphirane **1** points to the O atom as the harder nucleophilic center, bearing the highest negative (natural) electric charge (q^N = −0.671 au) with regard to the P atom (q^N = +0.738 au), as clearly observed in the electrostatic potential (ESP) map (Figure 1a). The latter center holds the uppermost natural atomic orbitals;[38] indeed the HOMO can be roughly described as a $\pi^*(3p_{(P)}\text{-}2p_{(O)})$ orbital with larger coefficients at P (Figure 1b) and whose bonding combination (π) is HOMO−2.

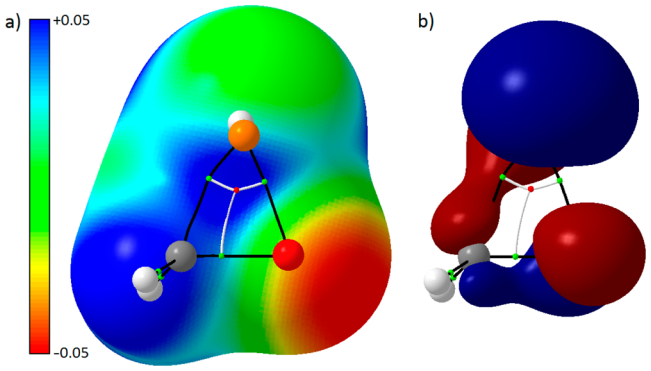
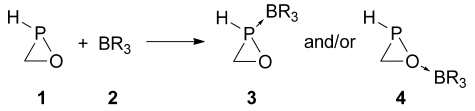


Figure 1. Computed (a) ESP map (from −0.05 au to +0.05 au) onto an electron density isosurface (0.06 au) and (b) Kohn–Sham isosurface of HOMO (0.06 isovalue) for **1**. Bond critical points (green) and the ring critical point (red) are shown as small spheres, together with bond paths (black) and paths connecting ring and bond critical points (white).

Scheme 2. Formation of Oxaphosphirane *P*- and *O*-Borane Complexes



a	R = H
b	R = Me
c	R = Ph
d	R = C_6F_5
e	R = C_6Cl_5
f	R = F
g	R = Cl
h	R = OH
i	R = OMe

Moreover, the theoretical underpinnings of the HSAB theory[39] allow quantification of the tendency of a particular Lewis acid to interact with different Lewis basic centers within a molecule. Thus, intrinsically related with HSAB theory definition are the concept of minimum quadratic difference in local softness,[40] $\Delta(s^2)_{kl}$, or the analogous quadratic difference in local philicity, $\Delta(\omega^2)_{kl}$,[41] which have also been successfully employed in organophosphorus chemistry to explain regioselective behaviors.[42] The fact that the change in grand potential $\Delta\Omega_{kl}$ prefers to be as negative as possible in the equilibrium at the final, equalized chemical potential (μ)[43] has also been used as a criterion to predict regioselectivity.[42a,44] In the comparative study of the interaction of a series of boranes **2** toward H_2O and PH_3, as representatives of the simplest neutral O- and P-nucleophiles, a general preference for the reaction with PH_3 is observed, as only $B(OH)_3$ (**2i**) displays lower $\Delta(s^2)$, $\Delta(\omega^2)$,

dx.doi.org/10.1021/ic500536h | Inorg. Chem. 2014, 53, 6132–6140

Table 1. Computed (B3LYP/def2-TZVPP//B3LYP-D3/def2-TZVP) HSAB-Derived Parameters for the Interaction of 2 with PH_3, H_2O, and the P and O Atoms in 1

		$\Delta(s^2)$				$\Delta(\omega^2) \times 10^3$				$\Delta\Omega^b$			
	ω (ω_k)[a]	PH_3	H_2O	$P_{(1)}$	$O_{(1)}$	PH_3	H_2O	$P_{(1)}$	$O_{(1)}$	PH_3	H_2O	$P_{(1)}$	$O_{(1)}$
2a	0.17 (−0.20)	3.33	10.02	7.02	9.82	26.09	31.24	26.46	30.33	−3.91	−1.31	−1.47	−1.13
2b	0.08 (−0.06)	0.03	1.36	0.42	1.29	0.25	0.96	0.28	0.80	−0.30	−0.01	0.00	0.00
2c	0.14 (−0.06)	0.06	1.19	0.33	1.12	0.29	1.05	0.33	0.88	−0.40	−0.03	−0.01	−0.01
2d	0.27 (−0.24)	11.23	22.01	17.43	21.72	38.80	45.04	39.25	43.94	−3.01	−0.85	−0.93	−0.70
2e	0.24 (−0.14)	2.04	7.67	5.08	7.50	9.59	12.81	9.82	12.23	−1.75	−0.43	−0.43	−0.33
2f	0.11 (−0.17)	1.44	6.44	4.08	6.28	16.82	21.01	17.12	20.26	−3.56	−1.21	−1.34	−1.04
2g	0.15 (−0.12)	0.53	4.28	2.41	4.15	6.39	9.06	6.57	8.57	−1.92	−0.54	−0.54	−0.43
2h	0.08 (−0.08)	0.52	4.24	2.38	4.11	1.69	3.18	1.79	2.89	−0.45	−0.03	−0.01	−0.01
2i	0.05 (−0.01)	2.60	0.07	0.62	0.09	0.68	0.12	0.63	0.18	0.00	−0.07	−0.12	−0.11

[a]Global philicity; local value in parentheses. [b]kcal/mol.

Table 2. Dissociation Energies[a] Computed for Model *P*- and *O*-Borane Complexes[b]

	H_3B-PH_3	H_3B-OH_2	F_3B-PH_3	F_3B-OH_2
SCS-MP2/def2-QZVPP	18.25	7.38	1.61	4.15
LPNO/NCEPA1/def2-QZVPP	18.56	8.54	1.80	5.29
CCSD(T)/ano-pTZV	18.12	8.60	1.64	4.74

[a]In kcal/mol. [b]At the geometries and using the zero-point energy correction obtained at the B3LYP-D3/def2-TZVP level.

Table 3. Relative Thermochemical Data (kcal/mol) Computed (PWPB95-D3/def2-TZVPP//B3LYP-D3/def2-TZVP) for Reactions Depicted in Scheme 2[a]

	a	b	c	d	e	f	g	h	i
TS (1 + 2 − 3)	0.99	−0.02	−1.93	−6.84	N/A	−2.04	1.86	N/A	N/A
TS (1 + 2 − 4)	1.10	−2.78			N/A	−5.50	−3.64	N/A	N/A
3	−23.93	−1.64	−3.62	−12.61	N/A	−2.01[b]	−3.28	N/A	N/A
TS(3 − 4)	−0.51					−1.66			
4	−13.34	−2.32[b]	−4.78[b]	−7.99[b]	N/A	−8.48	−7.26	N/A	N/A
TS(3 − 7)	10.01					27.04			
7	−31.19	−20.67	−17.23	−13.42	−12.31	20.10	1.36	−16.20	22.01
TS(4 − 8)	−10.33					18.59			
8	−55.78	−45.04	−40.62	−36.78	−40.58	−20.95	−36.45	−50.77	−10.12
TS(3 − 9)	18.27					51.27			
9	−76.19	−62.29	−60.20	−60.51	−62.55	−14.58	−37.98	−49.20	−11.01
TS(3 − 10)	−3.84					32.59			
10	−28.30	−22.02	−22.86	−21.64	−20.65	−8.69	−19.67	−39.75	1.60

[a]Relative to isolated **1**+**2**. [b]No real covalent complexes **3** and **4** are formed, but van der Waals complexes (**1**·**2**) instead.

and $\Delta\Omega$ values for H_2O than for PH_3 (Table 1). The same general preference holds for the attack to the P versus the O atom in oxaphosphirane **1**, although numerical differences here are much lower. The largest charge-transfer related $\Delta\Omega$ values correspond to reactions with the highly unsaturated B atom in BH_3 (**2a**); also, **2f** and **2d** display significantly large values. Note the remarkably mismatching (high positive) $\Delta(s^2)$ and $\Delta(\omega^2)$ values found for the same three boranes, varying in the order **2d** > **2a** > **2f**, in line with the order of local philicity at B (ω_k) for the three most electrophilic boranes included in the present study (Table 1).

Dissociation Energies and Strengths of B−O and B−P Bonds. The relative energies of the B−O and B−P bonds in neutral borane complexes were explored first. Very interestingly, dissociation energies were found to be strongly dependent on the substitution pattern of the boranes. At the CCSD(T)/ano-pTZV//B3LYP-D3/def2-TZVP level, in the case of highly electrophilic borane BH_3 (**2a**), the model H_3B-PH_3 complex (**2a**·PH_3) turned out to have a remarkably higher dissociation energy than H_3B-OH_2 (**2a**·OH_2) (Table 2), in good agreement with previously reported values for related species;[45] the less electrophilic boron trifluoride BF_3 (**2f**) displays lower dissociation energies and varies in the inverse order for complexes F_3B-OH_2 and F_3B-PH_3. Similar values were obtained at the computationally less expensive LPNO/NCEPA1/def2-QZVPP and SCS-MP2/def2-QZVPP levels (Table 2).

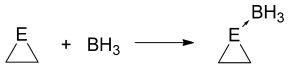
Borane derivatives **2e**, **2h**, and **2i** do not form stable acid−base adducts with oxaphosphirane **1**, but van der Waals complexes **1**·**2** instead. In agreement with the higher energy found for the B−P over the B−O bond in model complexes derived from BH_3 (**2a**) (vide supra), the oxaphosphirane *P*-complex **3a** is more stable than the *O*-complex **4a** (Table 3) and the same tendency is observed for **3d**/**4d**. In all other less electrophilic borane derivatives, complexation is shifted toward the *O*-complex **4** (Table 3), which parallels the above-mentioned higher dissociation energy of the B−O bond in BF_3-derived model complexes. However, the higher stabilization of *O*- (**4**) over *P*-complexes (**3**) must be viewed as a sum of energetic contributions and not only due to a comparison of

dx.doi.org/10.1021/ic500536h | Inorg. Chem. 2014, 53, 6132−6140

O−B versus P−B bond energies (vide infra). Stabilization of **3a,d** over **4a,d** might also be related with the fact that these substituents (at boron) are the least electron releasing ones (weaker donors).

In order to compare with the only reported borane complex of a three-membered phosphorus heterocycle,[17] the model phosphirane **5a** and its *P*-borane complex **6a** were also computed at the same level of theory (Scheme 3). For

Scheme 3. Formation of Phosphirane and Oxirane Borane Complexes 6a,b



5a E = PH **2a** **6a** E = PH
5b E = O **6b** E = O

completion, parent oxirane (**5b**) and its *O*-borane complex (**6b**) were considered as models for the few reported examples of this type of complex.[46] Here, the complexation energies for **5a** (−22.14 kcal/mol) and **5b** (−9.15 kcal/mol) were found to be similar to those for the formation of **3a** and **4a**, respectively (Table 3). The energy for the complexation of **5b** with BF_3 was reported to be 13.11 kcal/mol at the BSSE- and ZPE-corrected MP2/6-311++G(3df,2pd) level of theory, but only 5.18 kcal/mol with the lower quality 6-31G(d) basis set.[53]

Preferential stabilization of one or the other of the two isomers **3** and **4** might also be partly related with different strength of the B−E bonds (E: P or O). Among several possible bond-strength related descriptors, the electron density at bond critical points (BCP), $\rho(\mathbf{r})$, derived from Bader's atoms-in-molecules (AIM) theory,[32] has been successfully used in quantifying many different bonding situations.[12,47] On the other hand, two of the so-called "bond order" quantities, such as the Wiberg's bond index (WBI)[48] resulting from the Natural Bond Orbital (NBO) analysis,[36] and the Mayer's bond order (MBO),[49] are in widespread use. Also, the compliance matrix[50] approach offers a unique numerically stable (transferable) description of bond strength and subsequently bond orders.[51] The *relaxed force constants*, k_o,[49c,52] are computed as the reciprocal numerical values of the compliance constants C_{ii}, the diagonal elements of the compliance matrix. They are typically expressed in mdyn·Å^{-1} and measure the force required to distort a coordinate by a unit (force) amount while allowing all other coordinates to relax, i.e., its intrinsic stiffness (not depending on the bonding environment). From inspection of B−E bond strength parameters (Table 4) it can be observed that most complexes **3**, except **3f**, exhibit strong B−P bonds (**3a** ≈ **3g** > **3d** ≈ **3b** ≥ **3c**). The B−P bond in **6a** ($\rho(\mathbf{r})$ = 10.68 × 10^{-2} e/a_0^3; WBI = 0.964; MBO = 0.786; k_o = 1.421 mdyn/Å) turned out to be slightly weaker than that found in **3a**. On the contrary, only **4g**, and to some extent **4a** and **4f**, show moderately robust B−O bonds. This is in line with the moderate strength found for the computationally reported oxirane complex[53] and herein computed complex **6b** ($\rho(\mathbf{r})$ = 8.28 × 10^{-2} e/a_0^3; WBI = 0.491; MBO = 0.506; k_o = 1.027 mdyn/Å), so the latter have only a slightly stronger B−O bond than in **4a**.

Ring Strain Energies. The main feature related with the reactivity of these and many other three-membered heterocyclic systems is the ring strain that provides the driving force for the evolution to ring-opening products.[54] The RSE was computed using similar homodesmotic reactions (Scheme 4) to those reported for related oxaphosphirane and azaphosphiridine systems (see Computational Details).[9,11,55]

The RSE computed for **1** was found to be halfway between those of phosphirane **5a** (reported value 19.4 kcal/mol at CCSD(T)/def2-TZVPP; 19.2 kcal/mol at MP2/def2-TZVPP)[11a] and oxirane **5b** (reported value of 26.4 at the CCSD(T)/def2-TZVPP level;[9] 25.7 kcal/mol at the CBS-APNO level[56]) (Table 5). It increased significantly (+37.2% at the LPNO/NCEPA1 level) upon *P*-complexation with BH_3 (**3a**), while it slightly decreased (−7.7%) in the *O*-complex **4a**. The same tendency is observed for the Lagrange kinetic energy at the ring critical point (RCP), $G(\mathbf{r})$, that was recently shown to correlate well with RSE within related systems,[57] at much lower computational cost, and also successfully employed within the oxaphosphirane series.[55] By using this computationally inexpensive $G(\mathbf{r})$ quantity, the ring strain in *P*-complexed oxaphosphiranes **3** is observed to increase with respect to the uncomplexed ring system **1** (0.1584), in agreement with RSE values, and varying in the order **3c** (0.1617) ≤ **3b** (0.1621) ≤ **3f** (0.1628) < **3a** (0.1658) ≪ **3d** (0.1730) < **3g** (0.1751). The above-mentioned decrease of RSE upon *O*-complexation also correlates with lower $G(\mathbf{r})$ values for **4**, following the sequence **4d** (0.1556) ≫ **4f** (0.1496) ≈ **4b** (0.1494) ≥ **4c** (0.1482) ≥ **4g** (0.1470) ≫ **4a** (0.1403). As expected, phosphirane **5a** exhibits even lower $G(\mathbf{r})$ value (0.0894) that increases remarkably (7.6%) upon *P*-complexation to **6a** (0.0978), whereas oxirane **5b** displays the highest value (0.2067) only slightly decreased upon *O*-complexation to **6b** (0.2010).

It is worth mentioning that despite the HSAB-derived parameters (Table 1) and the E−B bond strength related descriptors (Table 4) point to a most favorable interaction of boron with the P atom in comparison with the O atom in oxaphosphiranes **1** (this also holds for the interaction with the P atom in phosphirane **5a** in comparison with the O atom in oxirane **5b**), the difference in complexation energies leading to *P*- or *O*-complexes (**3** and **4**, respectively) (Table 3) is the property that determines the regioselectivity, which not always suggests a preferred *P*-complexation. The discrepancy arises from the counterbalancing effect of the destabilization coming from the required rehybridization process at the donor atom and, on the other hand, the increase of ring strain systematically induced by *P*-complexation, in contrast to the relief of ring strain that is associated with *O*-complexation.

The above-mentioned increase in ring strain upon *P*-complexation could also be interpreted qualitatively in terms of a change of the hybridization at phosphorus. According to NBO analysis, the lone pair at the P atom in **1** is located in an almost nonhybridized 3s (69.42% of s-character) atomic orbital (AO), while using formally pure 3p AOs in all three covalent bonds to H (87.16% p), C (88.70% p), and O (90.19% p). Using **3a** for comparative purposes, formation of the P−B bond promotes a formal sp^3 hybridization at P that uses AO with higher p-character in the formally dative bond to B (55.44% p), and comparatively lower p-character in its covalent bond to H (76.39 p %) and, particularly, in endocyclic bonds to C (80.38 p %) and O (83.51 p %). The increase in $\%s^{endo}$ at P requires accommodation of a larger endocyclic bond angle which causes the ring strain to rise.[54]

These data pave the way for a potential tuning in the tendency to favor ring-opening paths resulting from *P*-borane complexation of **1** (vide infra) by appropriate choice of substitution at boron in **2**, with BCl_3 (**2g**) and $B(C_6F_5)_3$ (**2d**) being the most promising candidates. It is worth mentioning

dx.doi.org/10.1021/ic500536h | Inorg. Chem. 2014, 53, 6132−6140

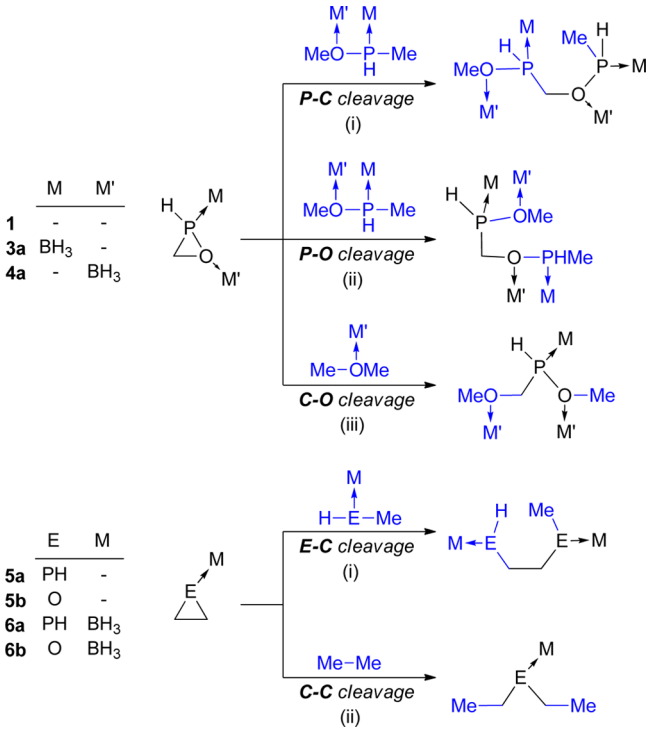
Table 4. Computed (B3LYP/def2-TZVPP//B3LYP-D3/def2-TZVP) Bond Strength Related Parameters for Endocyclic and E−B[a] and B−R Bonds in Oxaphosphirane 1 and Complexes 3 and 4

		a					b					c				
		P−C	P−O	C−O	E−B	%(B−R)[b]	P−C	P−O	C−O	E−B	%(B−R)[b]	P−C	P−O	C−O	E−B	%(B−R)[b]
1	$\rho(\mathbf{r})$[c]	15.02	14.99	25.61												
	WBI	0.975	0.800	0.986												
	MBO	1.056	1.009	0.963												
	k_o[d]	3.288	3.183	3.533												
3	$\rho(\mathbf{r})$ [c]	16.32	16.59	23.34	11.80	−14.0	16.06	16.19	23.74	9.13	−14.7	16.13	16.33	23.65	9.09	−13.6
	WBI	0.932	0.782	0.952	1.018	−3.6	0.946	0.790	0.956	0.812	−0.9	0.942	0.775	0.951	0.793	−2.1
	MBO	0.996	1.056	0.907	0.851	−8.2	1.013	1.038	0.913	0.609	−13.9	1.009	1.022	0.920	0.615	−14.1
	k_o[d]	3.884	3.914	2.878	1.740	−19.6	3.617	3.626	2.962	0.505	−30.7	3.588	3.577	2.943	0.382	−27.9
4	$\rho(\mathbf{r})$[c]	15.08	13.63	24.04	7.67	−9.5	14.94	14.59	25.26	1.45	−2.0	14.82	14.77	25.25	1.01	−1.3
	WBI	0.970	0.689	0.918	0.469	−0.5	0.973	0.777	0.973	0.065	−2.3	0.971	0.781	0.973	0.037	−3.7
	MBO	1.039	0.889	0.854	0.470	−0.6	1.054	0.992	0.918	<0.1	−2.4	1.049	1.001	0.913	0.103	−3.2
	k_o[d]	3.225	3.002	3.268	0.881	−14.5	3.287	3.154	3.514	0.013	−2.3	[e]	[e]	[e]	[e]	[e]
		d					**f**					**g**				
		P−C	P−O	C−O	E−B	%(B−R)[b]	P−C	P−O	C−O	E−B	%(B−R)[b]	P−C	P−O	C−O	E−B	%(B−R)[b]
3	$\rho(\mathbf{r})$[c]	16.63	17.11	23.35	9.19	−13.6	15.23	15.17	25.51	0.96	−0.6	16.85	17.16	23.20	11.73	−20.3
	WBI	0.947	0.806	0.945	0.801	−3.3	0.975	0.810	0.982	0.033	−1.1	0.951	0.805	0.944	0.828	−17.2
	MBO	1.011	1.105	0.885	0.603	−16.0	1.035	1.021	0.956	<0.1	−1.2	1.009	1.093	0.896	0.729	−19.8
	k_o[d]	3.834	4.130	2.764	0.704	−23.0	3.332	3.258	3.454	0.035	−0.8	3.869	4.057	2.717	1.077	−50.9
4	$\rho(\mathbf{r})$[c]	15.16	15.81	25.11	2.20	−2.2	15.32	13.72	24.14	6.68	−9.9	15.40	13.07	23.15	10.30	−15.8
	WBI	0.964	0.739	0.956	0.118	−5.0	0.971	0.701	0.927	0.303	−10.1	0.962	0.632	0.883	0.486	−16.9
	MBO	1.033	0.959	0.881	0.153	−4.6	1.038	0.898	0.856	0.441	−11.7	1.024	0.832	0.819	0.626	−16.4
	k_o[d]	3.294	3.142	3.501	0.024	−1.5	3.248	2.615	3.232	0.203	−38.2	3.140	2.456	3.054	0.842	−41.9

[a]E is P in **3** or O in **4**. [b]Percentage variation of the smallest value with respect to **2**. [c]$\times 10^2$ e/a_0^3. [d]mdyn/Å. [e]Not computed.

dx.doi.org/10.1021/ic500536h | Inorg. Chem. 2014, 53, 6132−6140

Scheme 4. Homodesmotic Reactions Used for the Calculation of RSE for Oxaphosphirane (1, 3a, and 4a), Phosphirane (5a and 6a), and Oxirane (5b and 6b) Derivatives



that this effect of ring strain increase in oxaphosphiranes upon *P*-borane complexation exceeds significantly the previously reported (scarce) effect observed for *P*-complexation by group 6 pentacarbonylmetal(0) units;[9] for the latter, little effect was also observed in the case of the related azaphosphiridine systems.[11]

Migratory Insertion/Ring-Opening Pathways. Migratory insertion/ring-opening is a long-known feature in the chemistry of epoxide borane complexes, but it was most often simply called epoxide reduction or hydroboration of epoxides.[58] In the present case both oxaphosphirane-borane complexes **3** and **4** exhibit a weakening of the B−R bonds as a consequence of the increase of electron density at the (newly created) borate centers. This in turn should enable migratory insertion of one of the R groups to one of the ring atom positions, thus resulting in a variety of possible ring-opening reactions (ROR). This type of process should be expected to be easier for complexes **3** due to their enhanced ring strain, as described beforehand.

The amount of electron density transferred from the oxaphosphirane to the borane unit, measured as the generated electric charge (Table 4), is notably higher in the case of the P-complexes **3**, especially for the cases of **3d**, **3g**, and **3a**, but almost vanishing for **3f** as expected for a van der Waals complex. This parallels the above-mentioned order for the strength of the P−B bonds (Table 4). With regard to O-complexes, only **4g**, **4a**, and **4f** exhibit moderate electron density transfer (Table 6) in agreement with the observed order of O−B bond strength (Table 4). The same holds true for **6a** and **6b**.

Table 6. Computed (B3LYP/def2-TZVPP//B3LYP-D3/def2-TZVP) Charge Transfer[a] Resulting from Oxaphosphirane-, Phosphirane-, and Oxirane-Borane Complexation

	a	b	c	d	f	g
3	0.638	0.577	0.596	0.661	0.021	0.658
4	0.258	0.042	0.030	0.081	0.177	0.272
6	0.613	0.274				

[a]Natural charges (au).

Indeed, all B−R bond strength parameters in **3** and **4** decrease with respect to the values for the boranes **2** (Table 4). In general the parameter showing the largest (negative) variation is the relaxed force constant, which could be tentatively interpreted in terms of a prevailing effect of increasing flexibility. *P*-Complexation (**1**→**3**) entails large B−R bond weakening, except for **3f**, due to its loose P···B interaction. The largest weakening is observed for **3g**, which adds to the above-mentioned large increase in RSE for the complexation **1**→**3g**. The boron-to-carbon [1,3] shift of the R group, affording acyclic isomers **7** via P−C bond cleavage (Scheme 5), is a process with moderate energy barrier, e.g., 33.94 kcal/mol for **3a**→**7a**, and exergonic in most cases (**7a**−**e**,**h**) (Table 3).

Scheme 5. Oxaphosphirane-Borane Complexes Isomerization and ROR Thereof

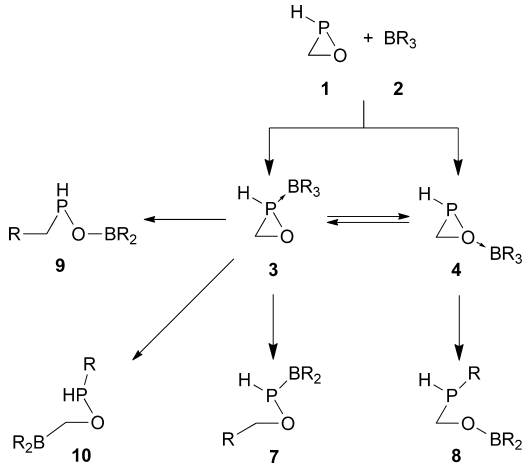


Table 5. Ring Strain Energies[a] Computed for Selected Three-Membered Heterocycles[b]

	1	3a	4a	5a	6a	5b	6b
PWBP95-D3	22.40	30.77	22.89	18.19	29.48	26.05	28.18
SCS-MP2	22.77	31.21	20.98	19.26	30.77	26.70	27.78
LPNO/NCEPA1	23.36	32.13	21.58	19.75	31.29	27.93	29.49

[a]In kcal/mol. [b]With the def2-TZVPP basis set, at the geometries and using the zero-point energy correction obtained at the B3LYP-D3/def2-TZVP level.

dx.doi.org/10.1021/ic500536h | *Inorg. Chem.* 2014, 53, 6132−6140

On the contrary, reduced B−R bond weakening is effected upon *O*-complexation except for **4g** and **4f** (Table 4), both being thermodynamically favored over their respective isomers **3** (Table 3). *O*-Complexes **4** also undergo a ROR via a boron-to-phosphorus [1,3] R group shift (P−O bond cleavage), leading to complexes **8** over a low barrier (3.01 kcal/mol for **4a**→**8a**) in a highly exergonic process.

A thorough exploration of the potential energy surface (PES) around complexes **3** and **4** reveals the existence of two accessible new open-chain isomers **9** and **10**. In almost all cases compounds **9** constitute the absolute energy minimum, except for **9h** and **9f** which are 1.57 and 6.37 kcal/mol higher in energy than **8h** and **8f**, respectively (Table 3). Although this seems to originate from **4**, via a [1,3] R B→C shift, a close inspection of the imaginary vibration mode associated with the TS of the formation of **9** unveils that it originates from **3** by means of concomitant [1,3] R B→C and [1,2] B P→O shifts. The rather high energy of this TS (42.20 kcal/mol for **3a**→**9a**) allows us to categorize **9** as the thermodynamically controlled product.

Finally a moderately exergonic process converts **3** into **10** by a concomitant [1,2] R B→P and [1,2] B P→C shifts following a path with rather low activation energy (22.23 kcal/mol for **3a**→**10a**).

CONCLUSIONS

This study presents a first-time-ever analysis of the formation and bonding of parent oxaphosphirane−borane complexes. It is predicted that the parent oxaphosphirane reacts with BR_3 derivatives **2** to form preferentially *P*-complexes involving the softer basic center (the P atom) according to DFT-based HSAB-related parameters, except for the case of $B(OMe)_3$ (**2i**) in which O-complexation seems to be preferred. This is in agreement with higher bond dissociation energies of P−B (**3**) over O−B bonds (**4**) only for BH_3 (**2a**) and $B(C_6F_5)_3$ (**2d**), the latter representing the cases with the least electron releasing substituents at boron within this test bed. In the same vein, an assessment using bond strength related parameters shows that most complexes **3**, except **3f** (R = F), exhibit strong P−B bonds (**3a** ≈ **3g** > **3d** ≈ **3b** ≥ **3c**), but only **4g** (R = Cl) and to some extent **4a** (R = H) and **4f** (R = F) show moderately robust O−B bonds.

A remarkable increase in the ring strain energy of phosphirane and oxaphosphiranes is observed upon *P*-complexation, especially in the case of **3g** and **3d**, whereas a moderate RSE decrease occurs in the case of *O*-complexation for both oxirane and oxaphosphiranes. This seems to be the counterbalancing effect that is opposed to a systematic higher P−B bond strength in comparison to the O−B bond, finally leading to the above-mentioned regioselectivity.

According to the amount of charge transfer from the oxaphosphirane to the borane moiety, B−R bonds get weakened and, hence, allow for migratory insertion/ring-opening reactions (= selective intramolecular bond activation) to occur: groups R migrate from boron to one of the ring atom positions. In the case of *P*-complexes, this is additionally promoted by a release of the (increased) ring strain.

In total, *P*-complexation by appropriately selected borane reagents BR_3 should enable activation of three-membered *P*-heterocycles in a specific intramolecular fashion and, hence, allow for novel transformations in boron−phosphorus chemistry.

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates and energies for all computed species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the DFG (STR 411/29-1 and 411/31-1) and COST action CM1302 "*SIPs*" is gratefully acknowledged.

DEDICATION

Dedicated to Professor François Mathey on the occasion of his 70th birthday.

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dx.doi.org/10.1021/ic500536h | *Inorg. Chem.* 2014, 53, 6132−6140