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Phosphorus Heterocycles

Carbaborane-Substituted 1,2-Diphosphetanes**

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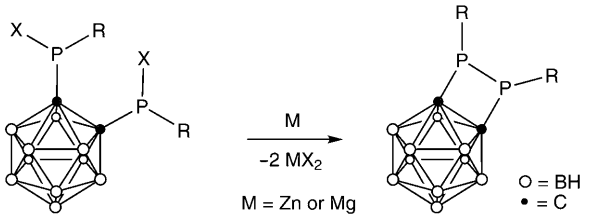
Strained phosphorus heterocycles have attracted considerable interest, not only because of their unusual reactivity and structures, but also as ligands for transition metals.[1] However, synthesis of stable four-membered phosphorus-containing heterocycles having an endocyclic P–P bond remains a challenge. Thus, 1,2-diphosphetanes are only accessible by [2+2] cycloaddition reactions, either by head-to-head dimerization of suitable phosphaalkenes,[2] or in rare cases by reaction of transition-metal-substituted diphosphenes with electron-deficient alkenes.[3] Major problems are often low yields and low purity of the products. Furthermore, 1,2-diphosphetanes are found only as side products or in a mixture of products but can rarely be obtained in pure form.[4] Therefore, the chemistry of these strained phosphorus heterocycles has hardly been explored.

Inspired by the unique electronic and structural properties of 1,2-dicarba-*closo*-dodecaborane(12) [*ortho*-carbaborane(12)][5] we have used bis(halophosphanyl)dicarba-*closo*-dodecaborane(12) compounds[6] as starting materials for facile synthesis of 1,2-diphosphetanes, specifically 1,2-bis-(chloro-*tert*-butylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) and 1,2-bis(bromo-*N*,*N*-diisopropylaminophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**2**), which are easily accessible by reaction of the dilithiated carbaborane with dichloro-*tert*-butylphosphine or dibromo-*N*,*N*-diisopropylaminophosphine.[6a,b] Reduction of a diastereomeric mixture of **1** or **2** with magnesium or zinc gave the 1,2-diphophetanes *rac*-**3** and *rac*-**4**, exclusively, in which the substituents have a *trans* arrangement (Scheme 1). The



rac-, *meso*-**1**: X = Cl; R = $C(CH_3)_3$ — *rac*-**3**: R = $C(CH_3)_3$
rac-, *meso*-**2**: X = Br; R = $N\{CH(CH_3)_2\}_2$ — *rac*-**4**: R = $N\{CH(CH_3)_2\}_2$

Scheme 1. Synthesis of 1,2-diphosphetanes *rac*-**3** and *rac*-**4**.

electron-withdrawing and electron-delocalizing ability of the cluster and the long C–C bond stabilize the four-membered diphospha heterocycles.[7] The air- and water-stable products *rac*-**3** and *rac*-**4** were isolated in high yield (98 and 80%, respectively).

In the $^{31}P\{^1H\}$ NMR spectra, a singlet is observed at $\delta =$ 41.3 (**3**) or 58.8 ppm (**4**). The $^{13}C\{^1H\}$ NMR spectra show a complex coupling pattern for an ABX spin system arising from the PCCP moiety at $\delta = 70.7$ (**3**) or 77.4 ppm (**4**) as reported earlier.[6b]

X-ray structure analysis[8] of **3** and **4** showed almost planar four-membered P_2C_2 rings, in contrast to [Fe(η^5-C_5Me_5)$(CO)_2$]-stabilized 1,2-diphosphetanes reported by weber et al. in 1990,[4] and *trans* orientation of the *tert*-butyl or amido substituents (Figure 1). The P–P bonds (2.246(3) Å (**3**), 2.263(1) Å (**4**); Table 1) are slightly longer than the standard value (2.22 Å),[9] while the P–C distances

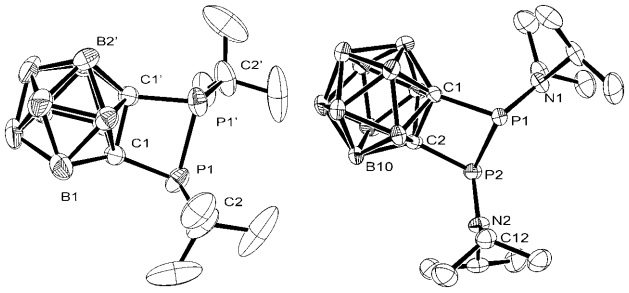


Figure 1. Molecular structures of carbaborane-substituted 1,2-diphosphetanes *rac*-**3** (left) and *rac*-**4** (right).

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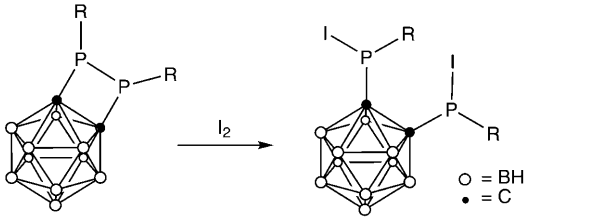
Table 1: Selected bond lengths [Å] and angles [°] of 1,2-diphosphetanes *rac*-**3** and *rac*-**4**.

Bond	**3**[a]	**4**
P–P	2.246(3)	2.263(1)
C_{carb}–C_{carb}	1.645(4)	1.631(5)
P–C_{carb}	1.883(2), 1.887(6)	1.913(4), 1.911(5)
C_{carb}-P-P	79.8(8), 80.4(2)	79.9(1), 79.7(1)
C_{carb}-C_{carb}-P	97.9(7), 97.6(2)	98.4(3), 98.8(3)
P-C_{carb}-C_{carb}-P	18.7	15.8

[a] Compound **3** is located on a C_2 axis but is completely disordered.

(1.883(6) Å (**3**), 1.913(4) Å (**4**)) compare well with similar bonds found in cyclic phosphanes.[10] The C_{carb}–C_{carb} bonds (1.645(4) Å (**3**), 1.631(5) Å (**4**)) are shorter than in the parent compounds **1** and **2** (Table 2). The P–N bond lengths (1.657(7) Å and 1.653(7) Å) are similar to those of the corresponding *ortho*-carbaborane derivatives.[6b] Both nitrogen atoms are coordinated in a trigonal-planar fashion.

Compounds **3** and **4** react with elemental iodine to give the first 1,2-bis(iodophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) compounds **5** and **6** (Scheme 2). In the case of **3**,



rac-**3**: R = $C(CH_3)_3$
rac-**4**: R = $N\{CH(CH_3)_2\}_2$

rac-**5**: R = $C(CH_3)_3$
rac-, *meso*-**6**: R = $N\{CH(CH_3)_2\}_2$

Scheme 2. Oxidative ring-opening reaction of *rac*-**3** and *rac*-**4** with elemental iodine.

the ring-opening reaction is diastereoselective to give the *rac* diastereomer **5** exclusively ($^{31}P\{^1H\}$ NMR: one singlet at $\delta =$ 98.4 ppm), while the reaction of **4** with iodine results in formation of both diastereomers ($^{31}P\{^1H\}$ NMR: two singlets at $\delta = 102.2$ and 102.0 ppm).

X-ray structural analyses[8] were carried out on *rac*-**5** and *rac*-**6** (Figure 2). The P–C and C–C bond lengths are similar

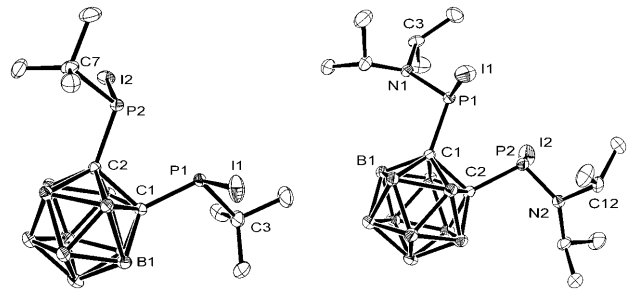


Figure 2. Molecular structure of *rac*-1,2-bis(iodo-*tert*-butylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**5**, left) and *rac*-1,2-bis(iodo-*N*,*N*-diisopropylaminophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**6**, right).

Table 2: Selected bond lengths [Å] and angles [°] of 1,2-bis(halophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s.

Bond	*rac*-**1**[6a]	*rac*-**2**[6b]	*rac*-**5**	*rac*-**6**
C_{carb}–P	1.892(2), 1.897(2)	1.901(2), 188.9(2)	1.892(2), 1.887(2)	1.898(2), 1.899(2)
C_{carb}–C_{carb}	1.770(2)	1.725(2)	1.765(3)	1.740(3)
P–Hal	2.074(9), 2.070(8)	2.260(1), 2.263(1)	2.455(1), 2.454(1)	2.506(1), 2.508(1)
C_{carb}-C_{carb}-P	112.1(1), 113.2(1)	111.6(1), 110.5(1)	112.1(1), 111.7(1)	110.8(1), 110.0(1)
C_{carb}-P-Hal	99.58(6), 99.66(6)	97.86(5), 98.36(5)	102.1(1), 102.3(1)	99.7(6), 98.36(5)

to those in **1** and **2** (Table 2). The P–I bonds are longer in comparison to the P–Cl bonds in **1** and P–Br bonds in **2**. In contrast to **3** and **4**, the orientation of the lone pairs of electrons at phosphorus in **5** and **6** suggests that they can act as chelate ligands in transition-metal complexes (P···P 3.207(1) and 3.107(1) Å for **5** and **6**, respectively).[11]

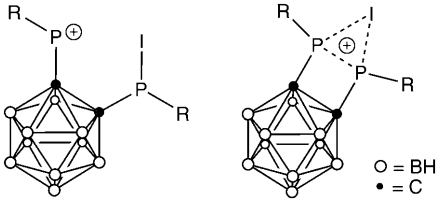
Density functional theory (DFT) calculations were performed to understand the different ring-opening behaviors of alkyl- and amido-substituted 1,2-diphosphetanes **3** and **4** with iodine (further details are given in the Supporting Information). All calculations were carried out with the hybrid B3LYP functional[12] of the Gaussian 09[13] program package and the 6-311G** basis set. The basis set for iodine was obtained from the EMSL Basis Set Library.[14]

The relative energies for all of the optimized structures are summarized in Table 3. The *rac* forms of **3** and **4** are clearly energetically favored by approximately 10 kcal mol^{-1} compared with the *meso* isomers, which is in agreement with the experiments. However, the energy difference between the *rac* and *meso* forms of **5** and **6** is too small (around 1 kcal mol^{-1}) to conclude an energetic preference for one of the isomers. Since these results do not yet explain the observed contrasting diastereoselective behavior, the transition states (TSs in Table 3) corresponding to the pyramidal inversion at one of the P atoms were located. Each transition state is characterized by one imaginary frequency corresponding to the normal mode associated with this conformational change (Table 3). The transition states for both reagents (**TS3**, **TS4**) and products (**TS5**, **TS6**) lie at significantly higher relative energies, which suggest a considerable energy barrier to inversion. Geometry optimizations of the *tert*-butyl-substituted intermediate structures suggest that the phosphonium (*trans*-**a**-$\mathbf{P}^+$ and *cis*-**a**-$\mathbf{P}^+$) structures are energetically more favored than their iodonium analogues (*trans*-**a**-$\mathbf{I}^+$ and *cis*-**a**-$\mathbf{I}^+$), while for the amido-substituted intermediates, the calculations show the iodonium structures (*trans*-**b**-$\mathbf{I}^+$ and *cis*-**b**-$\mathbf{I}^+$) to have the lower relative energies. However, the energy difference between the *trans*/*cis* forms of both alkyl- and amido-substituted intermediates is again insignificant (Table 3).

Transition states for inversion of both phosphonium and iodonium intermediates (Scheme 3) were also located. The energy barriers for inversion of the amido-substituted **TSb**-$\mathbf{P}^+$ and **TSb**-$\mathbf{I}^+$ are significantly lower than those predicted for the alkyl-substituted intermediates (**TSa**-$\mathbf{P}^+$ and **TSa**-$\mathbf{I}^+$), and

Table 3: Relative energies [kcal mol^{-1}] with zero-point vibrational energy (ZPE) corrections at the B3LYP/6-311G** level of theory (imaginary frequencies [cm^{-1}] in brackets).

Species	Relative energy	Species	Relative energy
rac-**3**	0	*rac*-**4**	0
meso-**3**	10.0	*meso*-**4**	11.9
TS3	36.5 [299*i*]	**TS4**	35.9 [294*i*]
rac-**5**	0	*rac*-**6**	0
meso-**5**	1.5	*meso*-**6**	1.1
TS5	51.3 [198*i*]	**TS6**	34.0 [311*i*]
trans-**a**-**P**$^+$	0	*trans*-**b**-**I**$^+$	0
cis-**a**-**P**$^+$	3.1	*cis*-**b**-**I**$^+$	0.5
cis-**a**-**I**$^+$	9.7	*trans*-**b**-**P**$^+$	2.8
trans-**a**-**I**$^+$	10.6	*cis*-**b**-**P**$^+$	5.3
TSa-**P**$^+$	27.9 [240*i*]	**TSb**-**P**$^+$	12.9 [16*i*]
TSa-**I**$^+$	50.2 [353*i*]	**TSb**-**I**$^+$	18.1 [29*i*]



Scheme 3. Ionic intermediates considered for theoretical studies.

they also exhibit lower imaginary frequencies (Table 3). Thus, inversion can take place at one of the P atoms in the amido-substituted intermediates, resulting in the experimentally observed *rac*/*meso* mixture of **6**, while the alkyl-substituted intermediates have higher energy barriers to such conformational changes. It has been shown for monoaminophosphane analogues[15] A_2PNB_2 that the anomeric effect can influence the inversion barrier.[16] Therefore, the $n_N \rightarrow \sigma^*_{(P\text{-}A)}$ interactions (identified with the NBO 3.1 code[17]) in the amido-substituted 1,2-diphosphetanes of our study, may be responsible for the observed lowering of the inversion barrier.

Development of a facile route to 1,2-diphosphetanes exploiting the unique electronic and structural properties of 1,2-dicarba-*closo*-dodecaborane(12) finally allows the reactivity of these unusual compounds to be investigated. Further studies are underway.

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