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Simulations Suggest Possible Triply Bonded Phosphorus $\equiv$ E13 Molecules (E13 = B, Al, Ga, In, and Tl)

Jia-Syun Lu, Ming-Chung Yang and Ming-Der Su

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Abstract

The effect of substitution on the potential energy surfaces of $RE_{13} \equiv PR$ ($E_{13} = B, Al, Ga, In, Tl$; $R = F, OH, H, CH_3, SiH_3, SiMe(Si^tBu)_2, Si^iPrDis_2, Tbt$, and Ar^*) is studied using density functional theory (M06-2X/Def2-TZVP, B3PW91/Def2-TZVP and B3LYP/LANL2DZ + dp). The theoretical results demonstrate that all triply bonded $RE_{13} \equiv PR$ compounds with small substituents are unstable and spontaneously rearrange to other doubly bonded isomers. That is, the smaller groups, such as $R = F, OH, H, CH_3$ and SiH_3 , neither kinetically nor thermodynamically stabilize the triply bonded $RE_{13} \equiv PR$ compounds. However, the triply bonded $R'E_{13} \equiv PR'$ molecules, possessing bulkier substituents ($R' = SiMe(Si^tBu)_2, Si^iPrDis_2, Tbt$ and Ar^*), are found to have a global minimum on the singlet potential energy surface. In particular, the bonding character of the $R'E_{13} \equiv PR'$ species is well defined by the valence-electron bonding model (model [II]). That is to say, $R'E_{13} \equiv PR'$ molecules that feature groups are regarded as $R'-E_{13} \equiv P-R'$. The theoretical evidence shows that both the electronic and the steric effects of bulkier substituent groups play a prominent role in rendering triply bonded $R'E_{13} \equiv PR'$ species synthetically accessible and isolable in a stable form.

Keywords: phosphorus, group 13 elements, triple bond, substituent effects, valence electrons

1. Introduction

Phosphorus is an interesting element, but many chemists have a poor comprehension of its bonding properties. Even though phosphorus and nitrogen belong to the same group in the periodic table, molecular nitrogen is a triply bonded diatomic molecule, but elemental white phosphorus is a tetrahedral compound wherein each atom is connected by three single bonds to the other atoms in the molecule. Phosphorus is usually connected to other elements by a

single chemical bond, which has been verified by lot of experimental evidences [1–14]. Also, molecules that feature a phosphorus double bond have been the subject of many experimental and theoretical studies of structure and reactivity [15–27]. However, little is known about the molecules that feature a phosphorus triple bond [28–32]. In particular, whether it is possible to anticipate the stability of the $R-E13 \equiv \text{phosphorus}-R$ ($E13 = B, Al, Ga, In, \text{ and } Tl$) species based on the effects of substituents, since the $R-E13 \equiv \text{phosphorus}-R$ systems are isoelectronic to the $R-E14 \equiv E14-R$ ($E14 = C, Si, Ge, Sn, \text{ and } Pb$) compound from the valence electron viewpoints.

This study uses the heavier acetylene analogue, $R-E13 \equiv P-R$ as a model molecule to determine the possibility of generating stable $RE13PR$ species that feature the $E13 \equiv P$ triple bond. In order to understand the effects of substituents on the stability of triply bonded $RE13 \equiv PR$ molecules, both small and bulky groups are chosen in this work. A better understanding of the bonding character and the structure of triply bonded $RE13 \equiv PR$ species will allow experimental chemists to discover novel and stable molecules that feature the $E13 \equiv P$ triple bond.

1.1. General considerations

This section uses a simple valence-electron bonding model to demonstrate the bonding nature of substituted triply bonded $RE13 \equiv PR$ compounds.

First, the $RE13 \equiv PR$ species is separated into two units: $R-E13$ and $R-P$. **Figure 1** shows that these two fragments represent two types of valence-electron bonding model (model [I] and model [II]). Therefore, the $R-E13$ moiety and the $R-P$ component have two and four valence electrons, respectively. The computational results show that the ground states of these two units are a singlet for $R-E13$ ($[R-E13]^1$) and a triplet for $R-P$ ($[R-P]^3$). Therefore, model [I] in **Figure 1** is considered as $[R-E13]^1 + [R-P]^1 \rightarrow [R-E13 \equiv P-R]^1$ and model [II] is given as $[R-E13]^3 + [R-P]^3 \rightarrow [R-E13 \equiv P-R]^1$.

If the excitation energy ($\Delta E1$) from the triplet ground state to the singlet excited state for $R-P$ is smaller than that for $R-E13$, then model [I] can be used to interpret the bonding character of $RE13 \equiv PR$. That is, model [I] demonstrates that the triple bond in $RE13 \equiv PR$ is a single donor-acceptor ($E13 \rightarrow P$) σ bond and two donor-acceptor ($E13 \leftarrow P$) π bonds. Therefore, the bonding character of $RE13 \equiv PR$ can be viewed as $RE13 \rightleftharpoons PR$. However, if the promotion energy ($\Delta E2$) from the singlet ground state to the triplet excited state for $R-E13$ is smaller than that for $R-P$, then model [II] can be used to explain the bonding character of $RE13 \equiv PR$. Namely, model [II] shows that the triple bond in $RE13 \equiv PR$ is a single traditional σ bond, a single traditional π bond and a single donor-acceptor ($E13 \leftarrow P$) π bond, so its bonding character can be viewed as $RE13 \rightleftharpoons PR$.

From model [I] and model [II] shown in **Figure 1**, two points need to be emphasized here. First, it is experimentally known that the covalent radius decreases as: Tl (148 pm) > In (142 pm) > Ga (122 pm) > Al (121 pm) > P (107 pm) > B (84 pm) [33]. Therefore, a large difference in the atomic radius results in a significant reduction in the overlap populations between $E13$ and phosphorus. Consequently, the bonding strength between phosphorus and the $E13$ element in the heteroatomic analogues of acetylene ($RE13 \equiv PR$) should be weak. Second, the π bond in the $RE13 \equiv PR$ species is also attributed to the lone pair of the $R-P$ moiety, which is donated into the empty $p-\pi$ orbital of the $R-E13$ unit. Since the lone pair of the $R-P$ component

Figure 1. The valence-bond bonding models ([I] and [II]) for the triply bonded $\text{RE}_{13}\equiv\text{PR}$ compound.

contains the s valence orbital of phosphorus and the p valence orbital of phosphorus is not the same size as that of the E13 atom, the overlap in the orbital populations between the P and E13 elements is small. In other words, on the basis of the bonding models that are shown in **Figure 1**, the triple bond between E13 and phosphorus is predicted to be very weak.

The computational evidences for these predictions are given in the following sections.

2. Results and discussion

2.1. Small ligands on substituted $\text{RE13} \equiv \text{PR}$

Five small substituents (R), including F, OH, H, CH_3 and SiH_3 , are initially chosen for this study. Three types of density functional theory (DFT) (M06-2X/Def2-TZVP, B3PW91/Def2-TZVP and B3LYP/LANL2DZ + dp) are used to determine the relative stability of the triply bonded $\text{RE13} \equiv \text{PR}$ species and its corresponding doubly bonded isomers ($\text{R}_2\text{E13} = \text{P}$: and: $\text{E13} = \text{PR}_2$). In other words, two types of the 1,2-substituent-shift reactions ($\text{RE13} \equiv \text{PR} \rightarrow \text{TS1} \rightarrow \text{R}_2\text{E13} = \text{P}$: and: $\text{RE13} \equiv \text{PR} \rightarrow \text{TS2} \rightarrow \text{E13} = \text{PR}_2$) are studied. The respective computational results for $\text{RB} \equiv \text{PR}$ [28], $\text{RAl} \equiv \text{PR}$ [29], $\text{RGa} \equiv \text{PR}$ [30], $\text{RIn} \equiv \text{PR}$ [31], and $\text{RTl} \equiv \text{PR}$ [32] are schematically shown in **Figures 2–6**.

The computational results that are shown in **Figures 2–6** show that regardless of the type of small substituent that is chosen, the triply bonded $\text{RE13} \equiv \text{PR}$ compound cannot be stabilized on the 1,2-migration energy surfaces. That is to say, it is easy for the RE13PR species to migrate to the corresponding doubly bonded $\text{R}_2\text{E13} = \text{P}$: or: $\text{E13} = \text{PR}_2$ isomers rather than to the triply bonded $\text{RE13} \equiv \text{PR}$ molecules. The theoretical evidence strongly suggests that the experimental detection of $\text{RE13} \equiv \text{PR}$ that features small groups is very unlikely so they are not discussed in this section [28–32].

2.2. Large ligands on substituted $\text{R'E13} \equiv \text{PR'}$

Four bulky groups (R') are used to study the effects of substituents on the triply bonded $\text{RE13} \equiv \text{PR}$ molecules. These are $\text{SiMe}(\text{Si}^t\text{Bu}_3)_2$, $\text{Si}^i\text{PrDis}_2$, Tbt ($\text{C}_6\text{H}_2\text{--}2,4,6\text{--}\{\text{CH}(\text{SiMe}_3)_2\}_3$) and Ar^* ($\text{C}_6\text{H}_3\text{--}2,6\text{--}(\text{C}_6\text{H}_2\text{--}2,4,6\text{--}i\text{Pr}_3)_2$) [34, 35]. In order to avoid the London dispersion forces [36], the dispersion-corrected M06-2X/Def2-TZVP level of theory [37] is used to compute geometrical parameters and some properties. The respective results for $\text{RB} \equiv \text{PR}$ [28], $\text{RAl} \equiv \text{PR}$ [29], $\text{RGa} \equiv \text{PR}$ [30], $\text{RIn} \equiv \text{PR}$ [31], and $\text{RTl} \equiv \text{PR}$ [32] are shown in **Tables 1–5**. The same level of theory is also used to determine the feasibility of producing triply bonded $\text{R'E13} \equiv \text{PR'}$ compounds (**Scheme 1** and **Tables 1–5**).

1. For bulky groups (R'), the $\text{E13} \equiv \text{P}$ triple bond distances ($\text{\AA}$) are anticipated to be in the range, 1.736–2.023 ($\text{B} \equiv \text{P}$), 2.152–2.183 ($\text{Al} \equiv \text{P}$), 2.146–2.183 ($\text{Ga} \equiv \text{P}$), 2.215–2.362 ($\text{In} \equiv \text{P}$) and 2.336–2.386 ($\text{Tl} \equiv \text{P}$).
2. The computed reaction enthalpies (ΔH1 and ΔH2) that are shown in **Scheme 1** and **Tables 1–5** show that regardless of the bulky ligand that is chosen, the energy of the triply bonded $\text{R'E13} \equiv \text{PR'}$ species is much lower than those of its corresponding doubly bonded $\text{R'_2E13} = \text{P}$: or: $\text{E13} = \text{PR'_2}$ isomers. This computational evidence indicates that sterically congested ligands kinetically stabilize the triply bonded $\text{R'E13} \equiv \text{PR'}$ compound.
3. The theoretical data in **Tables 1–5** show that the R' -E13 moiety has a singlet ground state, but the R' -P component has a triplet ground state. The production of the triply bonded

Figure 2. The relative Gibbs free energy surfaces for $RB \equiv PR$ ($R = H, F, OH, SiH_3$, and CH_3). These energies are calculated in kcal/mol and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ + dp levels of theory.

M06-2X/Def2-TZVP
B3PW91/Def2-TZVP
B3LYP/LANL2DZ+dp

Figure 3. The relative Gibbs free energy surfaces for $\text{RAl} \equiv \text{PR}$ ($\text{R} = \text{H, F, OH, SiH}_3, \text{ and } \text{CH}_3$). These energies are calculated in kcal/mol and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ + dp levels of theory.

Figure 4. The relative Gibbs free energy surfaces for R-Ga ≡ P-R (R = H, F, OH, SiH₃, and CH₃). These energies are calculated in kcal/mol and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ + dp levels of theory.

Figure 5. The relative Gibbs free energy surfaces for $\text{RIn}\equiv\text{PR}$ ($\text{R} = \text{H}, \text{F}, \text{OH}, \text{SiH}_3$, and CH_3). These energies are calculated in kcal/mol and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ + dp levels of theory.

Figure 6. The relative Gibbs free energy surfaces for $\text{RTl} \equiv \text{PR}$ ($\text{R} = \text{H, F, OH, SiH}_3, \text{ and CH}_3$). These energies are calculated in kcal/mol and are calculated at the M06-2X/Def2-TZVP, B3PW91/Def2-TZVP, and B3LYP/LANL2DZ + dp levels of theory.

$R'E13 \equiv PR'$ compound at the singlet ground state constitutes a combination of two triplet units, $[R'-E13]^3$ and $[R'-P]^3$. Therefore, using the information in **Figure 1**, the bonding nature of the $E13 \equiv P$ triple bond in $R'E13 \equiv PR'$ can be regarded as $RE13 \equiv PR$.

4. The theoretical analyses in Section II shows that the bond order for the $E13 \equiv P$ triple bond should be very weak. **Tables 1–5** show that the Wiberg bond indices (WBI) [28, 39] for $RE13 \equiv PR$ compounds that feature sterically bulky substituents are all a little greater than 2.0. The theoretical evidence demonstrates that $RE13 \equiv PR$ that features bulky groups has only a weak triple bond because the WBI for the $C \equiv C$ bond in acetylene is computed to be 2.99.

The results of this study show that successful schemes for the synthesis and isolation of triply bonded $RE13 \equiv PR$ molecules are imminent.

R'	SiMe(Si ^t Bu ₃) ₂	Si ⁱ PrDis ₂	Tbt	Ar*
B $\equiv$ P(Å)	1.736	2.021	2.023	2.021
$\angle R'-B-P$ (°)	157.2	166.0	164.4	166.6
$\angle B-P-R'$ (°)	122.0	112.5	121.3	123.3
$\angle R'-B-P-R'$ (°)	174.7	165.5	168.9	169.5
Q _B ¹	−0.2574	−0.1395	0.2718	0.3520
Q _P ²	−0.1824	−0.3922	0.2260	0.2522
$\Delta EB'$ for R'-B (kcal/mol) ³	25.92	24.86	28.76	34.64
$\Delta EP'$ for R'-P (kcal/mol) ⁴	−33.10	−37.47	−29.74	−30.52
HOMO-LUMO (kcal/mol)	73.76	43.44	47.10	41.60
BE (kcal/mol) ⁵	89.54	90.37	85.42	71.43
ΔH_1 (kcal/mol) ⁶	73.75	86.65	87.89	87.59
ΔH_2 (kcal/mol) ⁶	80.53	77.67	101.7	88.01
WBI ⁷	2.388	2.152	1.963	1.966

¹The natural charge density on the boron atom.

²The natural charge density on the phosphorus atom.

³ $\Delta EB'$ (kcal mol^{−1}) = E(triplet state for R'-B)−E(singlet state for R'-B).

⁴ $\Delta EP'$ (kcal mol^{−1}) = E(triplet state for R'-P)−E(singlet state for R'-P).

⁵BE (kcal mol^{−1}) = E(triplet state for R'-B) + E(triplet state for R'-P)−E(singlet for R'B $\equiv$ PR').

⁶See **Scheme 1**.

⁷The Wiberg bond index (WBI) for the B $\equiv$ P bond: see references [38, 39].

Table 1. The bond lengths (Å), bond angles (°), singlet-triplet energy splitting ($\Delta EB'$ and $\Delta EP'$), natural charge densities (Q_B and Q_P), binding energies (BE), the Wiberg bond index (WBI), HOMO-LUMO energy gaps, and some reaction enthalpies for R'B $\equiv$ PR' at the M06-2X/Def2-TZVP level of theory.

R'	SiMe(Si ^t Bu ₃) ₂	Si ⁱ PrDis ₂	Tbt	Ar*
Al ≡ P (Å)	2.168	2.152	2.183	2.175
∠R'-Al-P (°)	166.5	163.4	165.0	167.3
∠Al-P-R' (°)	117.4	119.7	122.1	121.3
∠R'-Al-P-R' (°)	166.4	163.8	168.5	167.5
Q _{Al} ¹	0.9712	0.9210	1.1072	1.326
Q _P ²	-0.8751	-0.9674	-0.3430	-0.359
ΔE _{Al} ' for Al-R' (kcal/mol) ³	28.89	29.30	42.50	40.22
ΔE _P ' for P-R' (kcal/mol) ⁴	-23.10	-27.47	-30.51	-28.52
HOMO-LUMO (kcal/mol)	52.74	34.83	49.98	57.15
BE (kcal/mol) ⁵	43.49	54.96	47.51	35.41
ΔH ₁ (kcal/mol) ⁶	95.15	85.23	91.83	85.60
ΔH ₂ (kcal/mol) ⁶	96.13	82.75	90.56	85.31
WBI ⁷	1.572	1.592	1.685	1.534

¹The natural charge density on the aluminum atom.

²The natural charge density on the phosphorus atom.

³ΔE_{Al}' (kcal mol⁻¹) = E(triplet state for R'-Al)-E(singlet state for R'-Al).

⁴ΔE_P' (kcal mol⁻¹) = E(triplet state for R'-P)-E(singlet state for R'-P).

⁵BE (kcal mol⁻¹) = E(triplet state for R'-Al) + E(triplet state for R'-P)-E(singlet for R'Al≡PR').

⁶See **Scheme 1**.

⁷The Wiberg bond index (WBI) for the Al≡P bond: see reference [38, 39].

Table 2. The bond lengths (Å), bond angles (°), natural charge densities (Q_{Al}' and Q_P'), singlet-triplet energy splitting for Al-R' and P-R' units (ΔE_{Al}' and ΔE_P'), binding energies (BE), HOMO-LUMO energy gaps, Wiberg bond index (WBI), and some reaction enthalpies for R'Al ≡ PR' at the dispersion-corrected M06-2X/Def2-TZVP level of theory.

R'	SiMe(Si ^t Bu ₃) ₂	Si ⁱ PrDis ₂	Tbt	Ar*
Ga ≡ P (Å)	2.167	2.146	2.172	2.183
∠R'-Ga-P (°)	158.2	161.3	152.0	158.4
∠Ga-P-R' (°)	127.8	120.4	117.3	126.1
∠R'-Ga-P-R' (°)	176.0	175.5	169.4	166.9
Q _{Ga} ¹	0.8023	0.8266	0.8952	0.9003
Q _P ²	-0.7655	-0.7473	-0.8662	-0.8825
ΔE _{ST} for Ga-R' (kcal/mol) ³	30.71	31.34	34.08	38.35
ΔE _{ST} for P-R' (kcal/mol) ⁴	-23.10	-27.47	-23.51	-20.52
HOMO-LUMO (kcal/mol)	83.14	81.83	73.50	71.34
BE (kcal/mol) ⁵	91.53	102.9	85.34	89.46
ΔH ₁ (kcal/mol) ⁶	89.11	94.82	86.31	98.94

R'	SiMe(Si <i>t</i> Bu ₃) ₂	Si <i>i</i> PrDis ₂	Tbt	Ar*
ΔH ₂ (kcal/mol) ⁶	86.43	85.91	88.53	84.08
WBI ⁷	2.228	2.235	2.017	2.114

¹The natural charge density on the gallium atom.
²The natural charge density on the phosphorus atom.
³ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-Ga)-E(singlet state for R'-Ga).
⁴ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-P)-E(singlet state for R'-P).
⁵BE (kcal mol⁻¹) = E(triplet state for R'-Ga) + E(triplet state for R'-Ga)-E(singlet for R'Ga ≡ PR').
⁶See **Scheme 1**.
⁷The Wiberg bond index (WBI) for the Ga≡P bond: see reference [38, 39].

Table 3. The bond lengths (Å), bond angels (°), natural charge densities (QGa' and QP'), singlet-triplet energy splitting (ΔEST), binding energies (BE), the HOMO-LUMO energy gaps, the Wiberg bond index (WBI), and some reaction enthalpies for R'Ga ≡ PR' at the dispersion-corrected M06-2X/Def2-TZVP level of theory.

R'	SiMe(Si <i>t</i> Bu ₃) ₂	Si <i>i</i> PrDis ₂	Tbt	Ar*
InαP(Å)	2.362	2.337	2.215	2.238
∠R'-In-P (°)	169.6	175.0	177.9	171.4
∠In-P-R' (°)	115.0	112.0	113.2	115.1
∠R'-In-P-R' (°)	177.5	172.47	175.4	172.3
Q _{In} ¹	1.1046	0.9396	0.9489	0.9553
Q _P ²	-0.9546	-0.9363	-0.8560	-0.6715
ΔE _{ST} for In-R' (kcal/mol) ³	33.93	29.53	22.48	28.41
ΔE _{ST} for P-R' (kcal/mol) ⁴	-28.51	-27.58	-25.64	-22.31
HOMO-LUMO (kcal/mol)	74.96	72.41	87.56	88.43
BE (kcal/mol) ⁵	86.51	84.30	92.61	90.64
ΔH ₁ (kcal/mol) ⁶	92.07	90.08	97.41	87.46
ΔH ₂ (kcal/mol) ⁶	88.35	89.18	89.26	79.32
WBI ⁷	2.263	2.251	2.188	2.174

¹The natural charge density on the central indium atom.
²The natural charge density on the central phosphorus atom.
³ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-In)-E(singlet state for R'-In).
⁴ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-P)-E(singlet state for R'-P).
⁵BE (kcal mol⁻¹) = E(triplet state for R'-In) + E(triplet state for R'-P)-E(singlet for R'In ≡ PR').
⁶See **Scheme 1**.
⁷The Wiberg bond index (WBI) for the In≡P bond: see reference [38, 39].

Table 4. The bond lengths (Å), bond angels (°), singlet-triplet energy splitting (ΔEST), natural charge densities (QIn' and QP'), binding energies (BE), the HOMO-LUMO energy gaps, the Wiberg bond index (WBI), and some reaction enthalpies for R'In≡PR' at the B97-D3/LANL2DZ + dp level of theory.

R'	SiMe(Si ^t Bu ₃) ₂	Si ⁱ PrDis ₂	Tbt	Ar*
Tl ≡ P(Å)	2.386	2.384	2.385	2.336
∠R'-Tl-P (°)	166.9	166.4	168.9	161.2
∠Tl-P-R' (°)	122.3	113.7	116.2	115.6
∠R'-Tl-P-R' (°)	171.4	179.5	173.9	174.4
Q _{Tl} ¹	0.975	0.739	1.166	1.218
Q _P ²	-0.860	-0.826	-0.344	-0.257
ΔE _{ST} for Tl-R' (kcal/mol) ³	35.91	35.52	31.27	30.24
ΔE _{ST} for P-R' (kcal/mol) ⁴	-43.10	-37.47	-39.74	-40.52
HOMO-LUMO (kcal/mol)	71.27	27.21	58.05	39.34
BE (kcal/mol) ⁵	80.24	85.43	62.51	67.89
ΔH ₁ (kcal/mol) ⁶	91.34	90.49	89.22	87.11
ΔH ₂ (kcal/mol) ⁶	73.98	72.83	71.27	74.01
WBI ⁷	2.116	2.273	2.127	2.201

¹The natural charge density on the central thallium atom.

²The natural charge density on the central phosphorus atom.

³ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-Tl)-E(singlet state for R'-Tl).

⁴ΔE_{ST} (kcal mol⁻¹) = E(triplet state for R'-P)-E(singlet state for R'-P).

⁵BE (kcal mol⁻¹) = E(triplet state for R'-Tl) + E(singlet state for R'-P)-E(singlet for R'Tl ≡ PR').

⁶See Scheme 1.

⁷The Wiberg bond index (WBI) for the Tl≡P bond: see reference [38, 39].

Table 5. The bond lengths (Å), bond angles (°), singlet-triplet energy splitting (ΔE_{ST}), natural charge densities (Q_{Tl}¹ and Q_P²), binding energies (BE), the HOMO-LUMO energy gaps, the Wiberg bond index (WBI), and some reaction enthalpies for R'Tl ≡ PR' at the dispersion-corrected M06-2X/Def2-TZVP level of theory.

Scheme 1. Several important conclusions can be drawn from the results in Tables 1–5.

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