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A New Class of Azadipnictiridines Generated by an Unusual Rearrangement Reaction

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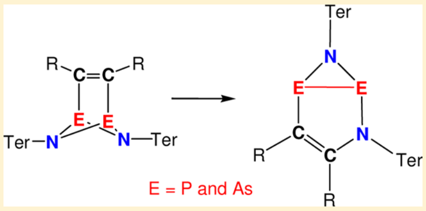
Ⓢ *Supporting Information*

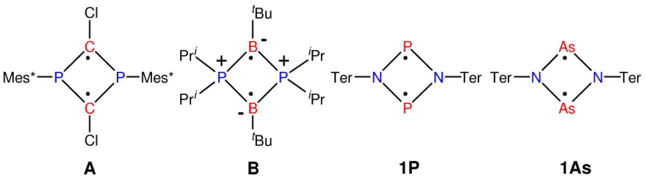
ABSTRACT: Dipnictadiazanediyls, $[E(\mu\text{-NR})]_2$ (E = P, As), the pnictogen analogues of cyclobutandiyl, were found to react readily with alkynes forming [2.1.1]bicyclic structures. These, in turn, rearrange in an unprecedented reaction to [3.1.0]bicycles leading to the isolation of the first azadiarsiridine and the determination of its solid-state structure. All new species were comprehensively characterized, and the reaction pathways and bonding situations were computationally studied.



■ INTRODUCTION

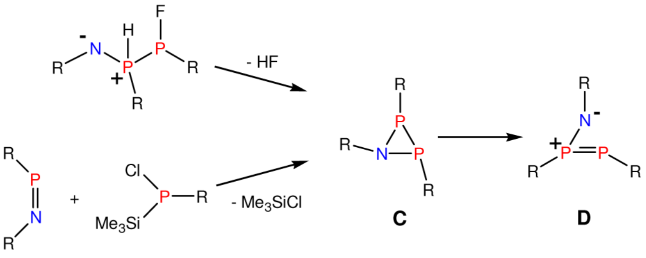
Because of their high reactivity, organic biradicals are mostly observed as transient, very short-lived species, which makes the detailed investigation of their chemistry rather difficult. Therefore, singlet biradicaloids, especially those derived from cyclobutanediyl, have attracted great interest in the past two decades because, by isolobal replacement of the carbon atom by other main group elements, there is a gain in stability at the cost of the loss of some biradical character.[1,2] Pioneering work in this field was carried out by the groups of Niecke,[3] Sita,[4] Power,[5,6] Lappert,[7] and Bertrand,[8] who successfully synthesized and characterized the first examples of such heteroatom-substituted biradicaloids (**A** and **B**, Scheme 1). Their reactivity has been explored toward bond-stretch isomerism,[9] ring-opening reactions,[10] polymerization,[11,12] reduction and oxidation,[13,14] photoinduced isomerization,[15] and reactions with small molecules.[16] Recently, following our interest in group 15 chemistry, we were able to prepare the first group 15 cyclic biradicaloid, a diphosphadiazanediyl,[17] and its heavier homologue, a diarsadiazanediyl.[18] These systems (**1P** and **1As**) are readily accessible by reductive dechlorination of the corresponding dichlorodipnictadiazanes. The incorporation of the bulky, yet flexible terphenyl[19−23] (Ter = 2,6-bis(2,4,6-trimethyl-phenyl)-phenyl) substituents on the N atoms within the molecule prevents dimerization and opens new possibilities for subsequent reactions.

Scheme 1. Selected Known Heterocyclobutanediyls (Ter = 2,6-bis(2,4,6-trimethyl-phenyl)-phenyl)



In the course of our investigations of the reactivity of these group 15 biradicaloids, the addition/activation of small molecules is a promising area[24] for the synthesis of small cage compounds. Promising candidates for addition to the biradicaloids are alkynes and especially thio-substituted alkynes.[25] Bis(alkylsulfanyl)acetylenes have shown a noticeable bias for cyclization reactions as well as for C_{sp}−S bond cleavage by transition metal complexes.[25−30] In this context, the target of the biradicaloid attack appeared as an open and interesting question. Accordingly, we report the unexpected formation of azadiphosphiridines by application of thio-substituted alkynes. $\lambda^3\lambda^3$-Azadiphosphiridines (**C**, Scheme 2) were first reported by Niecke et al. in 1981 and were prepared by elimination of HF from a linear P−P═N fragment.[31] The first solid-state structure of a $\lambda^3\lambda^3$-azadiphosphiridine was determined in the same year.[32] A greater variety of PPN ring substituents was obtained by reaction of phosphanediyls with iminophosphanes, which provides an elegant synthetic route to $\lambda^3\lambda^3$-azadiphosphiridines.[33,34]

Scheme 2. Preparation of $\lambda^3\lambda^3$-Azadiphosphiridines



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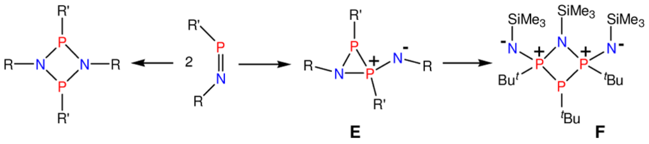
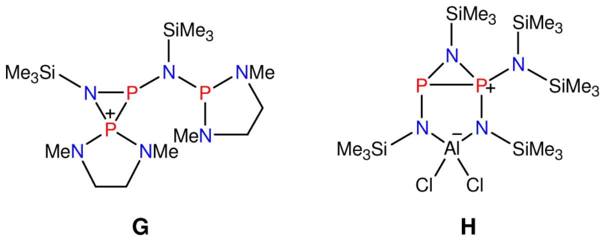
The intermediate formation of an iminodiphosphene that isomerizes upon addition of catalytic amounts of hexamethylphosphoramide (hmpa) with ring closure was assumed. Later, they were able to selectively carry out ring-opening reactions from $\lambda^3\lambda^3$-azadiphosphiridines, yielding iminodiphosphenes (**D**, Scheme 2).[35] Metal-coordinated $\lambda^3\lambda^3$-azadiphosphiridines were studied by Niecke et al., Danopoulos et al., and Roesky et al.[36−39]

Furthermore, Niecke et al. investigated the dimerization of iminophosphanes, which resulted in the [2 + 1] cycloaddition product $\lambda^3\lambda^5$-azadiphosphiridines (**E**, Scheme 3) instead of the thermodynamically more stable [2 + 2] cycloaddition product, cyclodiphosphadiazanes, if the substituents on P and N are *tert*-butyl groups.[40,41] NMR spectroscopic properties of $\lambda^3\lambda^5$-azadiphosphiridines have been studied by Wrackmeyer et al. and Gudat.[42,43] Such $\lambda^3\lambda^5$-azadiphosphiridines were found to incorporate even a third iminophosphane,[44] leading to the formation of an azatriphosphetidine (**F**, Scheme 3). Moreover, Niecke et al. found the isomerization reaction from $\lambda^3\lambda^3$-azadiphosphiridines to diphosphadiazanes to be catalyzed by Lewis or Brønsted acids.[45] A spirocyclic $\lambda^3\lambda^5$-azadiphosphiridinium cation was characterized by Sanchez et al.[46] who converted phosphonium cations with iminophosphanes to obtain the only isolable ionic derivative of azadiphosphiridines (**G**, Scheme 4). Gleiter et al. explored the electronic structure of azadiphosphiridines by photoeletron spectroscopy supported by computational studies.[47]

Scheme 3. Preparation of $\lambda^3\lambda^5$-Azadiphosphiridines



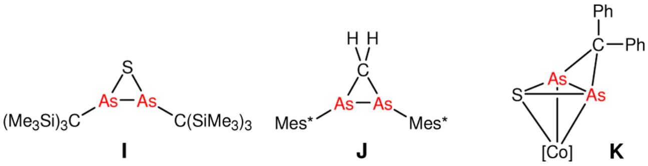
Scheme 4. Selected Azadiphosphiridines



In a more recent study, Burford et al. characterized the first [3.1.0]bicyclic $\lambda^3\lambda^5$-azadiphosphiridine (**H**, Scheme 4),[48] which was formally obtained by the reaction of 2 equiv of $(Me_3Si)_2NPN(SiMe_3)$ with $AlCl_3$ under elimination of 1 equiv of Me_3SiCl. The obtained azadiphosphiridine is remarkable in at least two ways, because (i) the P−P distance is the shortest so far observed for azadiphosphiridines and (ii) the P−P coupling is the weakest ($^1J_{PP}$ = −91 Hz, −63 °C; $^1J_{PP}$ = −94 Hz, +37 °C). Recently, $\lambda^3\lambda^5$-azadiphosphiridines were discussed as possible dimerization product for the iminophosphane $Mes^*NPC_6F_5$ (Mes* = 2,4,6-tris(*tert*-butyl)phenyl).[49]

Reports on three-membered heterocycles, which contain two arsenic atoms, are scarce. There are only three reports on such heterocycles, and these cover As_2S and As_2C rings (**I**−**K**, Scheme 5).[50−52] Yet, only the metal-coordinated As_2S three-membered ring is crystallographically characterized (**K**).[52]

Scheme 5. Known Carbon-Based Diarsiridines

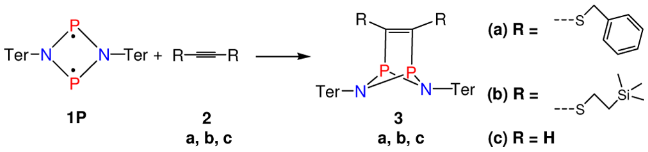


In this report we present novel $\lambda^3\lambda^3$-azadiphosphiridines. The new species were prepared utilizing an unprecedented rearrangement reaction from alkyne-bridged diphosphadiazanediyls. This type of reaction was then employed in the preparation of the first azadiarsiridine. All new compounds are comprehensively characterized by spectroscopic means and single-crystal X-ray diffraction. Finally, the rearrangement reaction and the bonding situation were computationally studied.

RESULTS AND DISCUSSION

Syntheses. Biradicaloids such as **1P** and **1As** can be used to activate small molecules bearing double or even triple bonds. The reactivity of sulfanylacetylenes[25] tempted us to carry out the conversion with biradicaloid **1P** (Scheme 6, Figure 1).

Scheme 6. Addition of Alkynes upon 1P



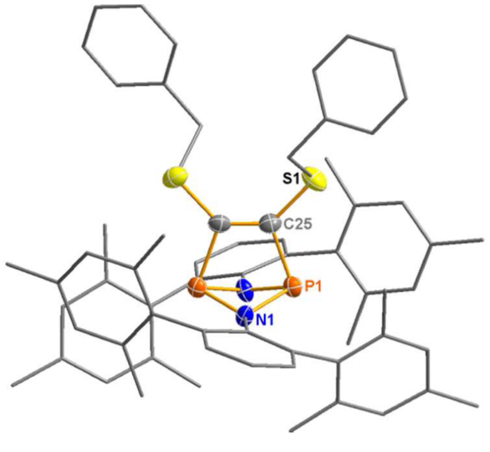
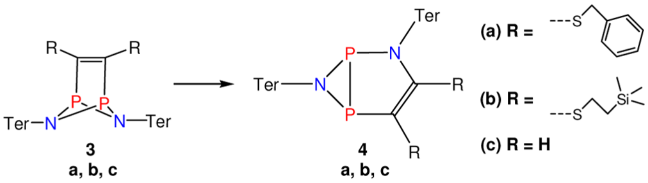


Figure 1. Molecular structure of **3a**. Thermal ellipsoids are drawn at 50% probability (173 K).[54]

Upon addition of bis(benzylsulfanyl)-acetylene **2a** to a solution of **1P**, an immediate change of color from orange to yellow was observed. The ^{31}P NMR spectrum of the reaction mixture after a short reaction time displayed a singlet at 232 ppm, which is 40 ppm upfield-shifted compared to that of **1P** (276 ppm), as expected for a transition from two-coordinate to three-coordinate phosphorus. The singlet in the ^{31}P NMR spectrum as well as the existence of only two resonances for the methyl groups of the terphenyl moiety in the ^1H and ^{13}C spectra (*ortho* and *para*) already indicated the formation of a symmetric molecule, **3a**. First attempts to crystallize **3a** took two weeks from a saturated benzene solution. X-ray diffraction analysis of colorless crystals formed revealed, however, the azadiphosphiridine **4a** (Scheme 7, Figure 2) to be the unexpected product.

Scheme 7. Rearrangement Reaction



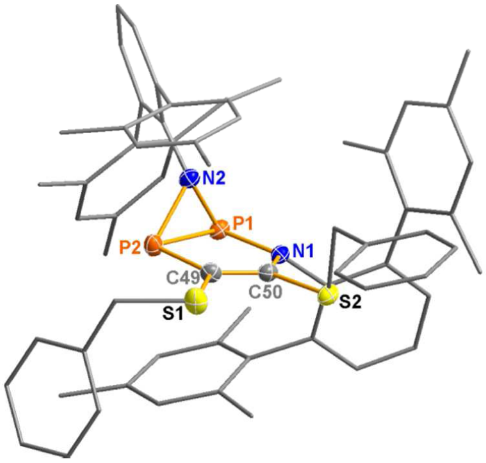


Figure 2. Molecular structure of **4a**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: P1–P2 2.2063(5), C49–C50 1.356(2), N1–P1–P2–C50 0.12(7); cf. Table 5.

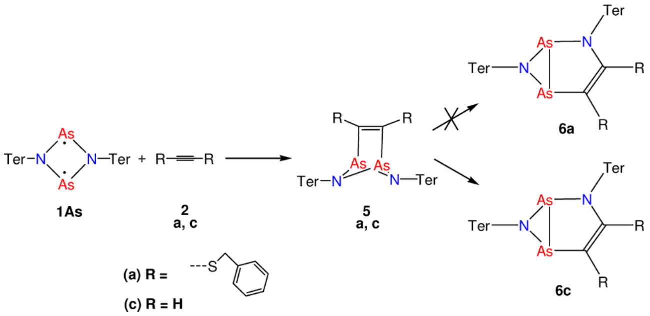
Additionally, the identity of the bulk sample as **4a** was also confirmed by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. The ^{31}P NMR spectrum consisted of an AB pattern ($^{1}J_{PP}$ = −113 Hz),[53] while ^{1}H and ^{13}C NMR spectra showed two inequivalent terphenyls. Further attempts of crystallization from freshly prepared **3a** were only partially successful: Any attempts lasting longer than 48 h exclusively yielded colorless crystals of **4a**, even when stored at −40 °C. The rearrangement was neither completely suppressible by lower temperature nor by the absence of light (Table 1).

Fast-grown crystals of **3a** were obtained from dichloromethane and benzene, but those crystals were strongly anisotropic needles and not suitable for structure elucidation. The crystals obtained from benzene at least allowed the determination of the unit cell. Crystals grown from *n*-hexane were of sufficient quality for X-ray diffraction experiments, but slowly decomposed on the goniometer, probably due to the loss of cocrystallized solvent molecules. Consequently, the obtained data set was poor, but at least confirmed the connectivity of **3a** (Figure 1).[54] These results prompted us to intensively study the reactivity of biradicaloids toward sulfanylacetylenes. The next step was to confirm this type of reaction, so another sulfanylacetylene, bis(2-trimethylsilylethylsulfanyl)-acetylene **2b**, was employed in the reaction. Again, the conversion readily occurred, and the recorded ^{31}P NMR spectrum showed the expected singlet at 231 ppm. In case of **3b**, the crystals grown overnight were even suitable for X-ray diffraction studies. In the supernatant, the beginning formation of azadiphosphiridine **4b** (Scheme 7) was observable by means of ^{31}P NMR spectroscopy (Table 1). The rearrangement to full conversion took four weeks at room temperature. Further effort was put into the investigation of the heavier congener, **5a** (Scheme 8).

Table 1. Selected ^{31}P and ^{1}H NMR Data (δ in ppm, *J* in Hz) for Monitoring the Rearrangement (bridged species left, rearranged right)[53]

	δ (^{31}P)		δ (P_C)	δ (P_N)	$^{1}J_{PP}$
3a	231.6	**4a**	−79.9	−55.7	−113
3b	230.7	**4b**	−76.7	−48.3	−102
3c	212.3	**4c**	−87.0	−60.4	−91
	δ (^{1}H)		δ (H_{CP})	δ (H_{CCP})	$^{3}J_{HH}$
3c	7.69	**4c**	4.10	6.15	6.7
5c	8.18	**6c**	4.40	6.56	6.8

Scheme 8. Alkyne Addition and Rearrangement with As Species



The conversion of **1As** with **2a** immediately led to a yellow solution (Scheme 8). After workup, nearly quantitative amounts of **5a** were isolated (Figure 3). NMR spectra confirmed the symmetric nature of the molecule. The unit cell of single crystals of **5a** grown from a benzene solution was isometric to the cell of **3a** when crystallized from benzene, thereby confirming the bridging mode for **3a** as well. But even

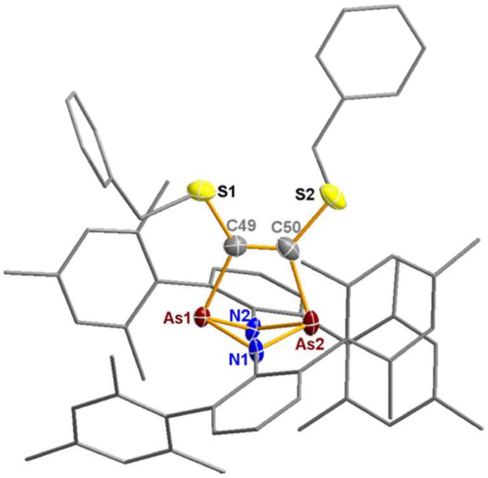


Figure 3. Molecular structure of **5a**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: As1–As2 2.7665(8), As1–C49 2.041(4), C49–C50 1.348(5), C49–S1 1.732(4), C49–As1–As2–C50 −3.2(2).

after two weeks, no indication of a rearrangement reaction for **5a** was spectroscopically observable. The differing behavior of the P compound **3a** and its corresponding As congener **5a** was supported by results of density functional theory (DFT) calculations.[55,56] These calculations revealed that azadiphosphiridine **4a** is 2.2 kcal·mol^{-1} more favorable than [2.1.1]-bicyclic **3a**, while for the analogous arsenic species **5a** is thermodynamically more stable than its azadiarsiridine isomer by 6.6 kcal·mol^{-1}. To evaluate the influence of the sulfanyl group on the rearrangement, respective calculations with acetylene were performed. As a result, the azaphosphiridine was predicted to be more stable than the bridged isomer, and thus, the rearrangement should be expected. Moreover, even for the heavier congener, the azadiarsiridine is thermodynamically more stable than the [2.1.1]bicylic isomer. Therefore, the rearrangement did not seem to be limited to thio-substituted alkynes. These results prompted us to carry out a last set of experiments with acetylene, initially yielding **3c** and **5c** (Schemes 6, 7, and 8). Both compounds were surprisingly insoluble in common solvents. **3c** and **5c** exhibited characteristic ^{1}H NMR spectra, with resonances at 7.7 and 8.2 ppm, respectively, caused by the H atoms of the C_2H_2 bridging moiety. When impure starting materials were employed in the reaction, for example, with $(TerNH)_2AsCl$ contaminated $[TerNAsCl]_2$, these impurities cocrystallized with the desired product **5c**. When kept in solution, the rearrangement reaction (Schemes 7 and 8) was observable via ^{1}H NMR spectroscopy, giving rise to resonances at 4.10 and 6.15 ppm for **4c** and at 4.40 and 6.56 ppm for **6c**, respectively (cf. Table 1). Unfortunately, the reaction proceeded very slowly. Any attempts of increasing the reaction rate by heating (above 50 °C) or ultraviolet irradiation decomposed **6c**, which is not stable in dichloromethane for a prolonged period, either. However, upon storage of a sample of **5c** in toluene at ambient temperature for seven weeks, eventually full conversion into **6c** was observed (Scheme 8).

Spectroscopic Properties. The new diphospha-diaza-[2.1.1]bicyclohexenes are symmetric, both terphenyl groups are equivalent in **3a**, **3b**, **3c**, **5a**, and **5c**, as indicated by ^{1}H and ^{13}C NMR spectra. In each, all *ortho* methyl groups exhibit one resonance, indicating the free rotation of the mesityl groups. This provides a difference to the previously investigated diazene or diphosphene bridged biradicaloids,[24] in which, owing to sterical congestion, there is an *endo-* and an *exo-ortho* methyl group. Furthermore, the bridging C atoms are found at low field as a doublet of doublets due to the coupling with both of the P nuclei (δ = 168.3 ppm (**3a**), 168.8 ppm (**3b**), 168.1 ppm (**3c**)) or as singlet for the arsenic species (δ = 172.6 ppm (**5a**), 171.4 ppm (**5c**)). The coupling constants are within the expected ranges for $^1J_{CP}$ and $^2J_{CP}$ coupling, but the bridging sulfanylacetylenes display stronger coupling ($^1J_{CP}$ = −78.1 Hz (**3a**), −73.6 Hz (**3b**), −59.4 Hz (**3c**), $^2J_{CP}$ = 9.4 Hz (**3a**), 9.2 Hz (**3b**), 6.6 Hz (**3c**)).[57,58] **3b** further exhibits an AA′XX′ pattern for the ethylene fragment. The coupling constants were determined for **3b** and for comparison for **2b** as well, because the resonances were reported as multiplets only (Table 2).[25] The signals appear to be broadened, probably due to small, but unresolved additional coupling to the P nuclei. Nevertheless, the changes in magnitude of the coupling constants are small.

The ^{31}P and ^{1}H NMR spectra of **3c** display an AA′XX′ pattern as well. Both are not superimposed by other resonances (δ(H) = 7.69 ppm, larger downfield-shift than any other here occurring aromatic proton), so coupling constants were obtainable. The simulation of the spectra yielded the coupling constants (Figure 4). Signs of the coupling constants were assigned as indicated by DFT calculations. The bridging C_2H_2 units in **5c** cause a singlet resonance at 8.18 ppm (cf. 2.01 in C_2H_2, 7.69 in **3c**).

Table 2. Selected Simulated NMR Parameters (δ in ppm, J in Hz) of 2b and 3b in C_6D_6[59]

	δ (H_A)	δ (H_X)	$J_{AA'}$	J_{AX}	$J_{AX'}$	$J_{XX'}$
2b	0.90	2.53	−14.1	13.0	4.8	−12.2
3b	0.76	2.73	−14.2	12.8	5.0	−11.1

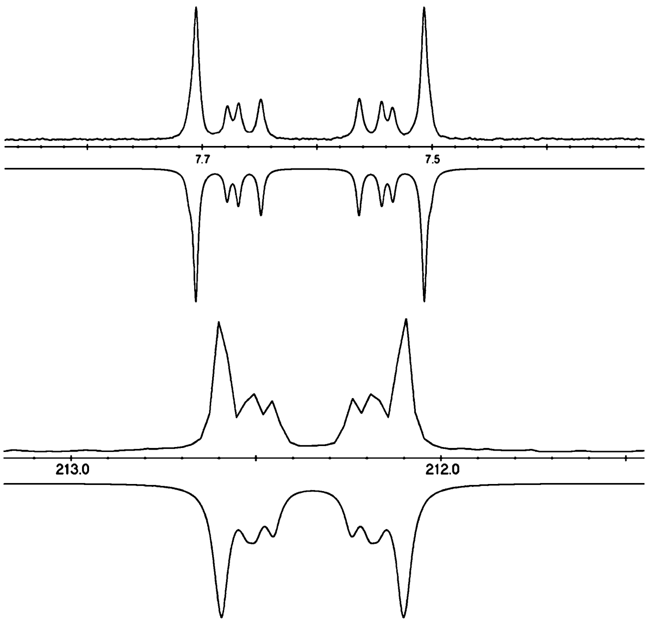


Figure 4. $P_2C_2H_2$ in **3c** ^{1}H (upper) and ^{31}P NMR (lower) spectrum of **3c**. $J_{HH'}$ = 7.9 Hz, J_{PH} = 9.7 Hz, $J_{PH'}$ = 50.0 Hz, $J_{PP'}$ = −10.9 Hz. δ(^{1}H) = 7.69 ppm, δ(^{31}P) = 212.3 ppm.

The rearrangement reaction can easily be monitored by ^{1}H or ^{31}P NMR spectroscopy (Table 1). The rearranged molecules show interesting NMR spectroscopic properties as well. The ^{31}P NMR spectrum contains the expected AB spin systems for **4a** (δ = −55.7, −79.9, $^1J_{PP}$ = −113 Hz), which compares well to the chemical shift of λ^3-P atoms in azadiphosphiridines.[31−34] The coupling is rather weak, the only weaker coupling is found in Burford's $\lambda^3\lambda^5$-azadiphosphiridine.[48] Because of the inequivalency of both terphenyl groups and the steric congestion, which prevents rotation, all methyl groups exhibit a separate singlet resonance in the ^{1}H NMR spectrum (Figure 5). Six of those are line broadened. The methylene protons of the benzyl groups are each observable as a doublet, since they are diastereotopic. These doublets occur at a wide range of chemical shifts (Figure 5): 2.73 (d, $^2J_{HH}$ = 11.1 Hz, 1 H, *pro-S*-PCS−CH_2), 3.49 (d, $^2J_{HH}$ = 11.1 Hz, 1 H, *pro-R*-PCS−CH_2), 3.54 (d, $^2J_{HH}$ = 11.6 Hz, 1 H, *pro-S*-NCS−CH_2), 4.20 (d, $^2J_{HH}$ = 11.6 Hz, 1 H, *pro-R*-NCS−CH_2).

4b has similar spectroscopic properties to **4a**, but the NMR spectra are even less clear. Ethylene group resonances are superimposed by methyl group resonances, so no coupling constants could be determined. **4c** exhibits an intriguing ABXY pattern. The P resonances are observed as a doublet, and a doublet of doublets of doublets, respectively, while the ^{1}H

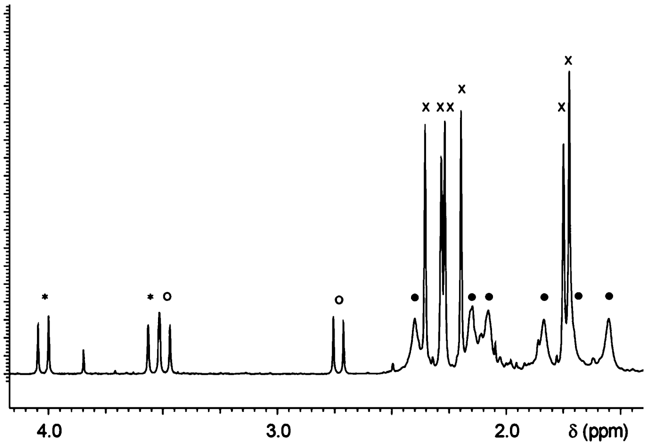


Figure 5. ^{1}H NMR spectrum in CD_2Cl_2 of **4a** displays resonances for the diastereotopic H atoms (* and ○) and six sharp (×) and six broad (●) singlets for methyl resonances in the range of 1.6–2.4 ppm.

resonances are a pseudo triplet and a doublet of doublets of doublets (Figure 6). Simulation of the spectra yielded all coupling constants (Table 3). $^1J_{PP}$ coupling is only −91 Hz at ambient temperatures, thereby being the smallest so far observed for azadiphosphiridines.

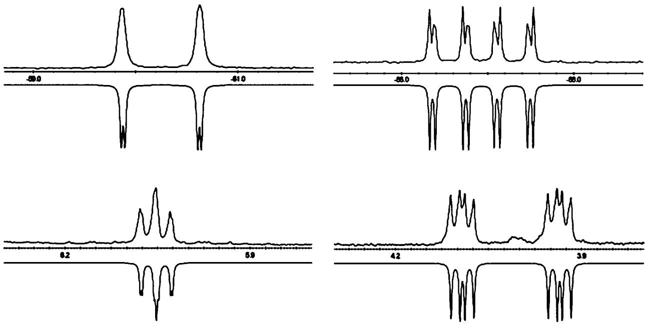


Figure 6. $P_2C_2H_2$ in **4c** ^{1}H (lower) and ^{31}P (upper) NMR spectra of **4c**.

Table 3. Selected NMR Parameters (δ in ppm, *J* in Hz) of 3c, Measured (Calculated)

	δ	$J(H_{C50})$	$J(H_{C49})$	J(P1)
H_{C50}	4.10			
H_{C49}	6.15	6.7 (7.8)		
P1	−60.4	4.4 (4.3)	−1.0 (−5.4)	
P2	−87.0	47.0 (41.7)	8.0 (1.9)	−91.0 (−67.0)

The formation of the first azadiarsiridine **6c** is also observable by ^{1}H NMR spectroscopy. The singlet resonance at 8.18 ppm disappears to give rise to two doublets at 4.40 and 6.56 ppm, respectively. The shift of both doublets is slightly more downfield than for the former acetylene protons of **4c**.

Solid-State Structures. **3b** and **5a** crystallize in the triclinic crystal system with four molecules per unit cell. In both cases, just one of the two individual molecules is employed for structural discussion, because the second molecule was found to be heavily disordered. In all of the structures of the [2.1.1]bicyclohexenes **3b**, **3c**, **5a**, and **5c**, the former planar biradicaloid is bent due to the addition of the alkyne (Figures 3, 7, and 8). The P–C and As–C bonds are longer than expected according to the sum of covalent radii for a single bond (Table 5, $\sum r_{cov}$(P–C) = 1.86 Å, (As–C) = 1.96 Å).[60] While the P–N and As–N bond lengths are well within the expected range for polar covalent bonds, there is a contraction of the P–P and As–As distance compared to the starting material (cf. P–P 2.6186(8) Å, As–As 2.8839(4) Å) caused by folding of the four-membered ring. In previous studies, this P–P contraction was observed for diazenes as bridging moieties as well and was attributed to the small bridging $(RN)_2$ entity, which shows in turn a comparatively long N–N bond.[24] But in contrast to the diazene, in **3a–c** the bridging C═C bond is not longer than the sum of covalent radii (1.34 Å). Within the bridging C_2H_2 moiety of **3c** and **5c**, the C–C bond is considerably shorter than expected for a double bond (**3c** C49–C50 1.306(4), Figure 8). On the other hand, in the sulfanyl derivatives **3b** (Figure 7) and **5a** (Figure 3) the corresponding C–C distance is in good accordance with a double bond (**3b** 1.351(4), **5a** 1.348(5) Å). This elongation of the C–C distance can be attributed to the adjacent S substituent, allowing electron delocalization, which causes the C–C bond to elongate and the C–S bond to contract compared to the sum of covalent radii ($\sum r_{cov}$ 1.78, **3b** C49–S1 1.743(3), **5a** C49–S1 1.732(4) Å),

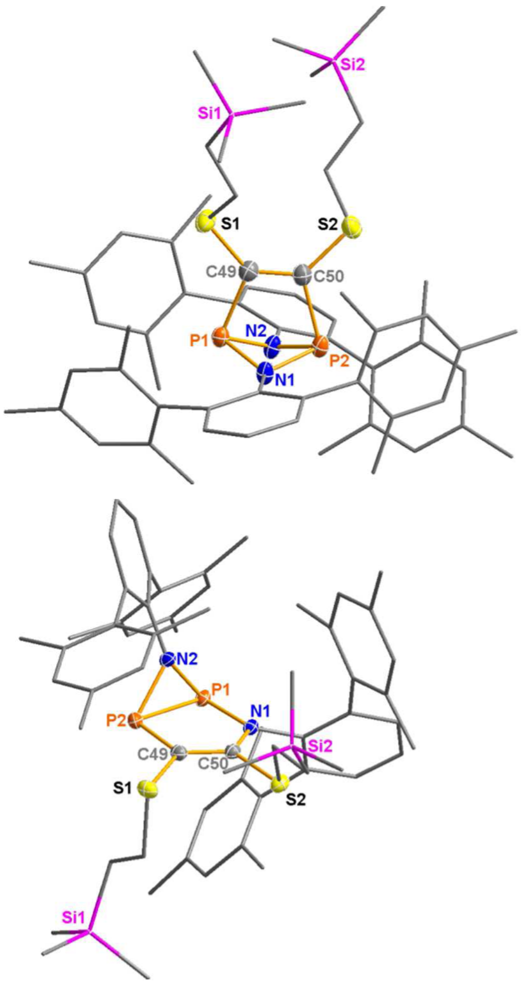


Figure 7. Molecular structures of **3b** (upper) and **4b** (lower). Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: **3b**: P1–P2 2.5299(9), P1–C49 1.904(3), C49–C50 1.351(4), C49–S1 1.743(3), C49–P1–P2–C50–2.7(1). **4b**: P1–P2 2.2234(5), C49–C50 1.374(2), N1–P1–P2–C49–0.97(4) ; cf. Tables 4 and 5.

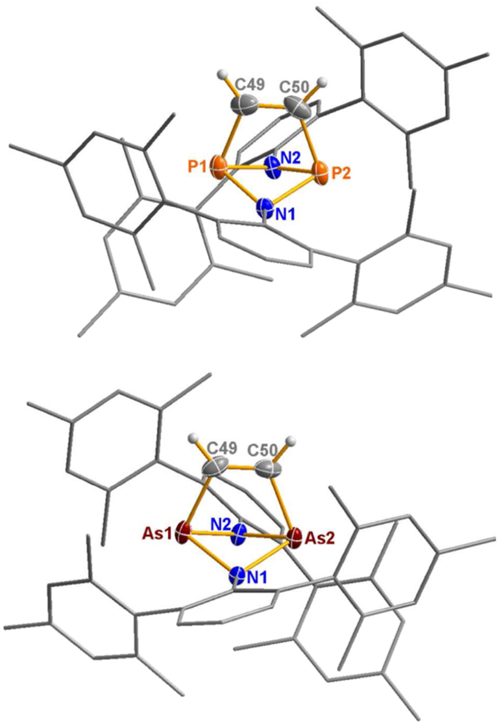


Figure 8. Molecular structure of **3c** (upper) and **5c** (lower). Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: **3c**: P1−P2 2.5235(6), P1−C49 1.883(2), C49−P1−P2−C50 0.69(9). **5c**: As1−As2 2.7611(4), As1−C49 2.008(2), C49−C50 1.306(4), C49−As1−As2−C50−0.8(1); cf. Table 4.

Table 5. Selected Structural Data of the Five-Membered Rings [Å][60]

	4a	4b	4c	$\sum r_{\mathrm{cov,E=E}}$	$\sum r_{\mathrm{cov,E\text{-}E}}$
C−C	1.356(2)	1.374(1)	1.346(2)	1.34	1.50
C−N	1.417(2)	1.395(1)	1.391(2)	1.27	1.46
P−C	1.809(1)	1.794(1)	1.793(1)	1.69	1.86
P−N	1.740(1)	1.770(1)	1.754(1)	1.62	1.82

even though this effect is diminished compared to the free alkyne (C−S 1.6756(9), C−C 1.215(2) Å).[29] In all cases, the former triple-bonded carbon atoms are now planar, as the angular sum is 359.7−359.9°.

The azadiphosphiridines **4a**, **4b**, and **4c** feature a consimilar geometry of the $P_2N_2C_2$ core (Figures 2, 7, and 9), which in turn consists of an azadiphosphiridine with an anellated P_2NC_2 moiety. This five-membered ring is planar, as proven by the sum of interior angles (**4a** 539.9°, **4b** 539.9°, **4c** 539.7°), which is very close to the expected value of 540° for a planar pentagon. The angle between the planes of the three-membered and the five-membered ring is nearly orthogonal (98.89(6)° **4a**, 102.51(3)° **4b**, 99.88(4)° **4c**).

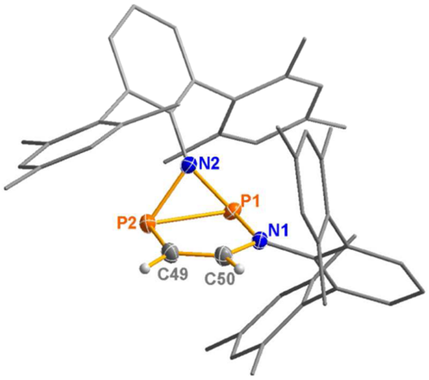


Figure 9. Molecular structure of **4c**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: P1−P2 2.2224(5), C49−C50 1.346(2), N1−P1−P2−C50 1.78(6); cf. Table 5.

In contrast to pyramidally configurated N2 ($\sum_{\mathrm{angles}}$ 337.3° (**4a**), 348.5° (**4b**), 340.8° (**4c**)), N1 is nearly planar coordinated ($\sum_{\mathrm{angles}}$ 351.5° (**4a**), 357.9° (**4b**), 358.8° (**4c**)), which is indicative of the aromatic character of the five-membered ring. N1 is nearest to planarity in **4c**, because the very small alkyne exhibits the least steric strain toward the terphenyl groups (Figure 9). The C atoms of the former alkynes bear no surprise; as expected for formally sp^2-hybridized atoms, the angular sum approaches 360° (C49 in **4a** 360.0°, **4b** 359.8°, **4c** 359.9°; C50 in **4a** 359.9°, **4b** 359.7°, **4c** 359.8°).

The P−P distance (**4a**: 2.2063(5) Å, **4b**: 2.2234(5) Å, **4c**: 2.2224(5) Å) corresponds very well with the expected value for a single bond ($\sum r_{\mathrm{cov}}$ = 2.22 Å)[60] and with the bond length observed by Niecke et al. for $\lambda^3\lambda^3$-azadiphosphiridines (P−P 2.211(2) Å in **C**, Scheme 2).[33,34] As is typical for delocalized double bonds, the bond lengths within the five-membered ring are in between the sum of covalent radii for a double and a single bond (Table 5).

The three-membered ring displays P−N distances consistent with polarized single bonds (**4a**: 1.710(1)/1.772(1) Å, **4b**: 1.709(1)/1.749(1) Å, **4c**: 1.718(1)/1.761(1) Å) that are elongated compared with the azadiphosphiridine reported by Niecke et al. (cf. **C**, Scheme 2, 1.698(4)/1.710(4) Å).[33] Nevertheless, as $\lambda^3\lambda^3$-azadiphosphiridines, the N atom is located quite central above the P−P bond, in contrast to $\lambda^3\lambda^5$-azadiphosphiridines, where it would be much closer to the λ^5-P atom, as for instance in Burford's azadiphosphiridine (**H**, Scheme 4, 1.637(2)/1.874(2) Å).[48]

The first azadiarsiridine **6c** (Figure 10) crystallizes from toluene in the space group $P\bar{1}$ without cocrystallized solvent molecules as also observed for isotypic **4c**. The As−As distance

Table 4. Structural Parameters of [2.1.1]Bicyclohexenes (distances in Å, angles in deg)

	3a[54]	3b	3c	5a	5c
Pn−Pn	2.595(2)	2.5299(9)	2.5235(6)	2.7665(8)	2.7611(4)
Pn−N[a]	1.755	1.759	1.754	1.899	1.895
Pn−C	1.906(3)	1.908(3)	1.887(2)	2.024(4)	2.008(3)
C−C	1.380(6)	1.351(3)	1.317(3)	1.349(5)	1.307(4)
Σ∠C	360.0	359.9	359.9	359.9	359.7

[a] Averaged.

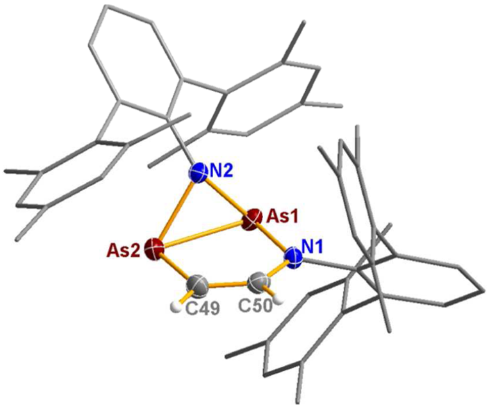


Figure 10. Molecular structure of **6c**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [deg]: As1–As2 2.4333(5), C49–C50 1.342(5), N1–As1–As2–C50 0.6(1); cf. Table 5.

(2.4333(5) Å) clearly resembles a single bond (cf. $\sum r_{\mathrm{cov}} = 2.42$ Å). This value deviates significantly from the As–As bond length of the only other crystallographically characterized carbon-based diarsiridine found by Couret et al. (cf. 2.850(3) Å in **K**, Scheme 3)[52] due to the metal coordination. In the same context, the authors noted elongated As–S (2.28 Å) and As–C (2.01 Å) bonds compared with the sum of covalent radii (2.23 and 1.96 Å). In contrast, the azadiarsiridine displays As–N bonds (1.896(2) Å and 1.924 Å) that compare well with the expected length of 1.92 Å. The As_2NC_2 ring is planar, with a sum of interior angles of 539.7°. Compared with **4c** the angle between the three-membered ring and the five-membered ring is slightly more acute (96.56(7)°).

Computations. A possible driving force in the rearrangement to the azadipnictiridine lies in the formation of two aromatic systems: the EEN-triangle (E = P or As) as well as the pentagon formed by EECCN are aromatic judged by NICS(0) calculations with values ranging from −27 to −25 ppm (for the three-membered ring) and −9 to −8 ppm (five-membered ring, cf. Table 6), respectively, provided the NICS(0) value for the three-membered ring is not influenced by the nearby electron density of the covalent bonds.[61] These values are comparable to the ones published for azulene, in which the five-membered ring has an NICS(0) value of −19.7 ppm and the seven-membered ring of only −7.0 ppm.[61] Despite both rings within the azadiphosphiridines being nearly perpendicular to each other, they form a common aromatic system.

Table 6. NICS(0) Values [ppm] of the Rearranged Species

	4a	4b	4c	6c
3-ring (ENN)[a]	−27.3	−25.8	−26.3	−25.5
5-ring (EECCN)	−9.4	−8.0	−8.2	−8.7

[a] E = P (**4a–c**) or As (**6c**).

The aromaticity indicated by the NICS(0) value of both the three-membered and the five-membered ring was more closely investigated by means of DFT calculations. While the three-membered ring could be a classic Hückel-aromatic system, involving two electrons (lone pair at N atom), the five-membered ring involves four electrons (C–C double bond and lone pair at N atom), which should render it antiaromatic.

The molecular orbitals of model compounds **4c_Me** and **6c_Me** (R = methyl in **4c** and **6c**) did not help to shed light on this matter, for they are strongly delocalized. Yet there is no purely bonding π-orbital, they all have at least one nodal plane perpendicular to the five-membered ring (Figure 11). The six π-electron aromaticity could be achieved, if the E–E bond is delocalized into the five-membered ring. Accordingly, natural resonance theory (NRT) analysis of, for example, **4c_Me** revealed four resonance structures among the 10 high-impact structures characterized by missing P–P bonds (cf. Scheme 9). Nevertheless, natural bond orbital (NBO) analysis found a P–P bond, which is dominated by contribution of p orbitals (NRT/Wiberg bond index for P–P bond = 0.91/0.94). The P–P bond is calculated to be bent from the line of nuclear centers by 32° (31° for **6c_Me**, Figure 11). This already indicates the banana shape of the bond, as it is discussed for other strained P molecules like P_4 as well.[62] However, this makes the bond a σ bond, so the bonding electrons should be unavailable for formal Hückel aromaticity. The picture of the electronic situation is finalized by electron localization function (ELF) calculations (Figure 11), clearly displaying a lack of electron density between the E atoms. Only a small disynaptic basin is found outside the E–E connection line in accord with the discussed NBO picture. This leads to the conclusion that the E–E banana bond can be referred to as a σ-type 2-electron-2-center bond bent out of the line of nuclear centers. Additionally, the molecule possesses a nonclassical aromatic system involving both heterocycles.

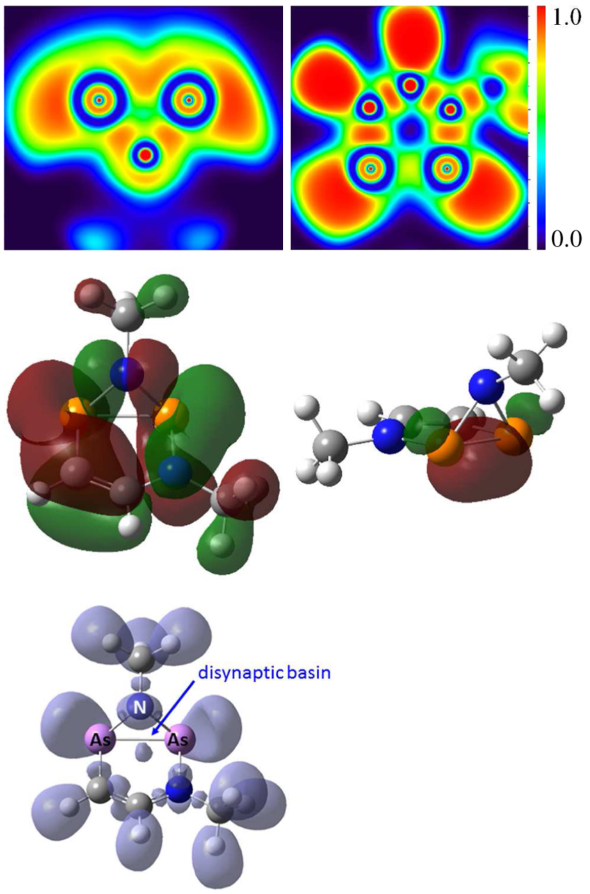
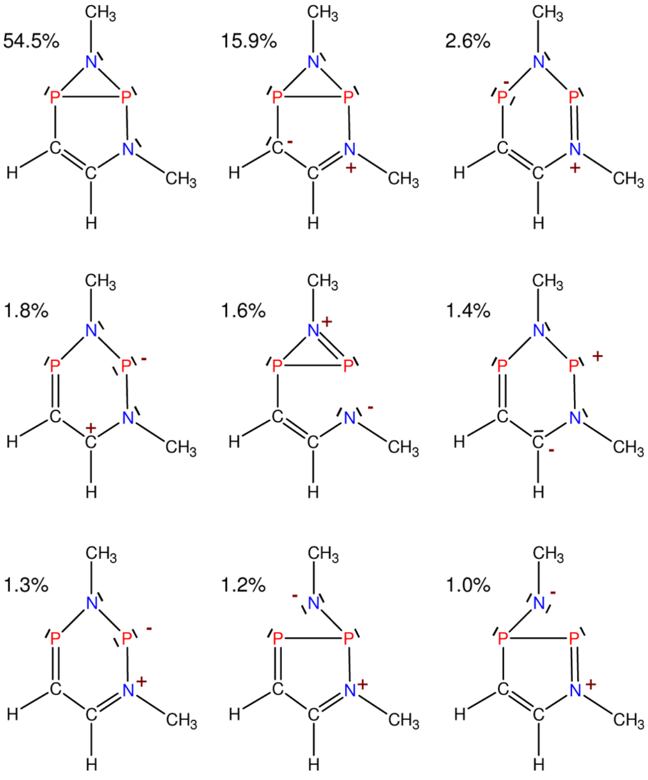


Figure 11. Electronic properties of **4c_Me** (upper left: ELF through the three-membered ring, right: through the five-membered ring; middle, left: HOMO, right: NBO P–P bond), and **6c_Me** (lower: ELF at 0.87).

Scheme 9. Lewis Representations Obtained by Natural Resonance Theory Calculations



Conclusions and Outlook. In summary, we presented the addition reaction of acetylene and respective disulfanylacetylenes on dipnictadiazanediyls **1P** and **1As**. Within these studies an unusual rearrangement reaction of initially formed hetero-[2.1.1]bicyclohexenes to [3.1.0]bicyclohexenes was uncovered. Finally, this rearrangement made the first azadiarsiridine **6c** accessible. The electronic features of the azadipnictiridines were studied, revealing a banana bond between the heavy pnictogens, which allows for the formation of a nonclassic aromatic system in both of the rings. Possible pathways for the rearrangement reaction were investigated by means of computation.

As supported by DFT calculations, this rearrangement reaction should render even the heavier azadipnictiridines accessible for analogous Sb and Bi species, which are unprecedented so far, as the azadipnictiridines are thermodynamically more stable by 8.8 kcal·mol^{-1} (Sb) and 3.8 kcal·mol^{-1} (Bi) than their [2.1.1]bicyclic isomers. Difficulties lie in the syntheses of the corresponding biradicaloids, for example, [TerNSb]$_2$ and [TerNBi]$_2$, which still remain unknown.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental information, syntheses, structure elucidation, computational details, and crystallographic data in CIF format. 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.

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