Heterocyclopentanediyls vs Heterocyclopentadienes: A Question of Silyl Group Migration

Henrik Beer, Jonas Bresien,* Dirk Michalik, Anne-Kristin Rölke, Axel Schulz,* Alexander Villinger, and Ronald Wustrack

Cite This: http	s://dx.doi.org/10.1021/acs.joc.0c0)0460	Read Online	-	
ACCESS	III Metrics & More		E Article Recommendations		s Supporting Information
ABSTRACT: The hypersilyl, (Me ₃ Si)	reaction of the singlet ₃ Si) with different isonitriles	biradica affordec	$[P(\mu-NHyp)]_2$ (Hyp = d a series of five-membered	diyl	diene

 N_2P_2C heterocycles. Depending on the steric bulk of the substituent at the isonitrile, migration of a Hyp group was observed, resulting in two structurally similar but electronically very different isomers. As evidenced by comprehensive spectroscopic and theoretical studies, the heterocyclopentadiene isomer may be regarded as a rather unreactive closed-shell singlet species with one localized N=P and one C=P double bond, whereas the heterocyclopentanediyl isomer represents an open-shell

singlet biradical with interesting photochemical properties, such as photoisomerization under irradiation with red light to a [2.1.0]-housane-type species.

INTRODUCTION

Biradicals (sometimes also called "biradicaloids" if the interaction between the two radical sites is significant) are an interesting research topic for both theoretical and synthetic chemists, as they exhibit unusual electronic structures, intriguing properties, and high reactivity.^{1–11} They are therefore worthwhile targets for the study of structure– property relationships, but their isolation is a challenge due to their intrinsic instability.

The high reactivity of biradicals arises from their characteristic electronic structure, which comprises two electrons in two (nearly) degenerate orbitals.¹ Thus, the electrons are strongly correlated (i.e., nondynamically or "statically" correlated), and multireference methods are needed to correctly describe the wave function of these systems.¹³ Depending on the magnitude and sign of the phenomenological Heisenberg exchange coupling constant $J = 1/2 \Delta E_{ST}$ ($\Delta E_{ST} = singlet$ triplet energy gap),^{14,15} the two electrons can either be ferromagnetically (I > 0) or antiferromagnetically (I < 0)coupled,⁸ resulting in a triplet or singlet ground state, respectively. Solely in the borderline case $J \approx 0$, a "perfect" biradical is formed, that is, a molecule with two independent radical centers (a so-called "two-doublet species"),¹⁵ which for all intents and purposes behaves like a radical species.³ In all other cases, one should note that the terms "biradical" or "biradicaloid" can sometimes be misleading, since the reactivity especially of singlet species may differ fundamentally from the reactivity of radicals (doublet species).

Here, we shall be only concerned with singlet biradicals (J < 0). It is vital to understand that in singlet biradicals, the spin density is exactly zero at every point in space. Thus, the reactivity of a singlet biradical may be very different from that

of a doublet radical or triplet biradical. Due to the near degeneracy of their frontier orbitals, singlet biradicals can easily undergo (cyclo)addition reactions (vide infra),³ which typically involve the interaction between HOMO and LUMO of the reaction partners.

The presence of heteroatoms such as N and P in cyclic biradicals tends to stabilize the singlet ground state by increasing the antiferromagnetic coupling (and thus decreasing the biradical character), resulting in improved stability. Sterically demanding substituents further provide kinetic protection, rendering the isolation of such species possible (Scheme 1).¹⁶⁻³¹ In particular, our own group could demonstrate the versatile reactivity of the stable fourmembered cyclic biradical $[P(\mu-NR)]_2$ (1, R = Ter [2,6-dimesitylphenyl] or Hyp [tris(trimethylsilyl)silyl]), which is based solely on group 15 elements (Scheme 2).³²⁻⁴⁰

Previously, we reported on the insertion of CO or isonitriles into one of the N–P bonds, leading to the formation of intensely colored, five-membered cyclic biradicals (e.g., heterocyclopentanediyls **2Ter**; Scheme 3).^{34,35} Only recently we could demonstrate that these five-membered ring systems are light-sensitive molecular switches^{41–45} that can be utilized to control a chemical equilibrium by turning the biradical character on and off (Scheme 3, right).⁴⁶

Special Issue: The New Golden Age of Organophosphorus Chemistry

Received: March 10, 2020 **Published:** May 12, 2020



Scheme 1. Some Examples of Open-Shell Singlet Biradicals Based on Four-Membered Main-Group Heterocycles



Scheme 2. Reactivity of Singlet Biradicals 1R^a



^{*a*}The reactions with S, Se, and multiple-bond systems (XCY) were reported for both R = Ter (1Ter) and R = Hyp (1Hyp). All other reactions were only investigated for the Ter system.

Scheme 3. Blue Heterocyclopentanediyls (2Ter-R^2) Are Formed by Insertion of Isonitriles into an NP Bond of Biradical 1Ter^a



^{*a*}Under irradiation, they isomerize to the closed-shell housane-type species 2'Ter-R² (R¹ = Ter; R² = *t*Bu, Dmp, Mes).

To explore the influence of the substituent R^1 at the N_2P_2 ring system on the reactivity, we started to investigate the analogous biradical system stabilized by Hyp groups (Hyp = $(Me_3Si)_3Si$, **1Hyp**).³⁹ Substitution of Ter by Hyp resulted in a larger charge transfer of electron density from the substituent R into the P_2N_2 ring (Ter 0.4 vs Hyp 1.2 *e*) and hence to a higher reactivity in case of **1Hyp**.³⁹ Of course, we were also interested in the possible utilization of this system as a molecular switch, so it was obvious to investigate its reactivity toward different isonitriles. However, contrary to aryl-based groups such as Ter, silyl groups such as Hyp can easily undergo rearrangement reactions,^{47,48} which turned out to play an important role in the outcome of the reactions in case of **1Hyp**.

RESULTS AND DISCUSSION

Reactions with Isonitriles. We started our investigation by treating the four-membered cyclic biradical $[P(\mu-NHyp)]_2$ (**1Hyp**) with the isonitriles *t*BuNC, DmpNC (Dmp = 2,6dimethylphenyl), MesNC (Mes = mesityl), and TerNC. To this end, a red solution of **1Hyp** in *n*-hexane was reacted with the respective isonitrile at ambient temperature (25 °C), resulting in an immediate color change to yellow (*t*Bu, Dmp, Mes) or dark blue (Ter). These different colors were somewhat unexpected, seeing that all reactions of the analogous biradical **1Ter** with isonitriles had resulted in blue heterocyclopentanediyls (**2Ter**-R², Scheme 3).

Crystallization of the products and subsequent single-crystal X-ray diffraction (SC-XRD) analysis revealed that in case of *t*BuNC, DmpNC, and MesNC, one Hyp group had 1,3-migrated from one of the nitrogen atoms in the five-membered ring system to the exocyclic nitrogen atom of the former isonitrile group (**3Hyp**-R², Scheme 4), resulting in the

Scheme 4. Reaction of 1Hyp ($R^1 = Hyp$) with Isonitriles (CN- R^2) Led to the Formation of Heterocyclopentanediyl 2Hyp-Ter or Heterocyclopentadienes 3Hyp- R^2 , Depending on the Steric Bulk of the Substituent R^2



formation of a heterocyclopentadiene rather than a heterocyclopentanediyl. Only in the case of TerNC, the expected product **2Hyp**-Ter was formed, as evidenced by ³¹P NMR and UV–vis spectroscopy (vide infra).

Molecular and Electronic Structures. Due to their similar structures, the dienes **3Hyp**-Dmp and **3Hyp**-Mes formed isomorphous crystals (space group: C2/c). Their congener **3Hyp**-*t*Bu crystallized in the space group $P2_12_12_1$ with a distinctly different unit cell (cf. Supporting Information (SI)). Still, the molecular structures of all three derivatives are similar with respect to the nearly planar five-membered N_2P_2C ring system and exocyclic N atom, with one Hyp substituent being connected directly to the ring system and the other being linked to the exocyclic N atom which also bears the *t*Bu, Dmp, or Mes group (Figure 1).

The structural parameters of the five-membered ring systems are nearly identical in all three cases (Table 1). All N–P, P–C, and C–N bond lengths range between typical single and double bonds (cf. $\sum r_{cov}$: N–P 1.82, N=P 1.62, P–C 1.86, P=C 1.69, C–N 1.46, C=N 1.27 Å),⁴⁹ indicating a delocalized π -bonding system.

Several attempts at crystallizing the blue Ter derivative **2Hyp**-Ter remained unsuccessful, due to its instability. Nonetheless, it could be unequivocally identified by NMR and UV–vis spectroscopy (vide infra). In the following, we will thus compare the calculated structures (PBE-D3/def2-SVP)^{50–52} of the isomers **3Hyp**-R² and **2Hyp**-R² (R² = Dmp, Mes, *t*Bu, Ter) to point out differences (Figure 2). First,



Figure 1. Molecular structures of **3Hyp**-Dmp, **3Hyp**-Mes, and **3Hyp**-*t*Bu in the crystal. Thermal ellipsoids set at 50% probability (123 K). Selected distances and angles can be found in Table 1.

Table 1. Selected Bond Lengths (Å) and Dihedral Angles (°) of 3Hyp-Dmp, 3Hyp-Mes, and 3Hyp-tBu in the Crystal

	3Hyp-Dmp	3Hyp-Mes	3Hyp-tBu
N1-P1	1.728(2)	1.726(1)	1.727(4)
N1-P2	1.663(2)	1.671(1)	1.670(4)
P1-C1	1.773(2)	1.777(2)	1.782(4)
P2-N2	1.617(2)	1.620(1)	1.612(4)
C1-N2	1.344(2)	1.345(2)	1.363(5)
C1-N3	1.376(2)	1.377(2)	1.371(5)
N1-P1-P2-N2	-179.8(1)	-179.6(1)	-179.0(3)
N1-P1-C1-N3	-179.0(1)	-178.1(1)	-179.2(4)



Figure 2. Calculated molecular structures of the experimentally observed species 3Hyp-Dmp and 2Hyp-Ter (PBE-D3/def2-SVP; cf. Tables S13 and S14).

it is worth noting that the calculated and experimental structures of **3Hyp**- R^2 (R^2 = Dmp, Mes, *t*Bu) are in reasonable agreement (mean difference in N-P/N-C/P-C bond lengths: 0.021 Å). When comparing the two sets of computed structures of $3Hyp-R^2$ and $2Hyp-R^2$, it becomes evident that in the case of $2Hyp-R^2$, both Hyp groups are attached to the ring system (N1, N2), as opposed to 3Hyp-R², where one Hyp substituent is connected to the exocyclic N3 atom. Furthermore, the P1-C1 (av. 1.84 Å), P2-N2 (av. 1.71 Å), and C1-N2 (av. 1.41 Å) bond lengths are significantly longer in **2Hyp**-R², now more in the range of polarized single bonds, whereas the C1-N3 bonds are shortened to an average of 1.30 Å, which corresponds to nearly isolated C=N double bonds. Thus, the bond lengths of both $2Hyp\text{-}R^2$ and $3Hyp\text{-}R^2$ are in nice agreement with the Lewis depictions in Scheme 4, indicating a rather different bonding situation in both species.

To compare the bonding situation in the cyclopentanediyl (2Hyp-R²) and cyclopentadiene derivatives (3Hyp-R²), calculations with the model systems 2SiH₃-Me and 3SiH₃-Me were performed. The calculated structural parameters of these models compare well with those of 2Hyp-R² and 3Hyp-R² (SI). CASSCF(8,6)⁵³⁻⁶¹ computations correlating all π

electrons were performed to investigate the biradical character of both isomers (Figure 3). The calculations indicate that the



Figure 3. Frontier orbitals of the cyclopentadiene $3SiH_3$ -Me and cyclopentanediyl $2SiH_3$ -Me (CAS(8,6)/def2-TZVP//PBE-D3/def2-SVP, isovalue = 0.03). Only the largest contributions to the wave function are shown. For a depiction of all active orbitals, please see SI, p. S4Sf.

wave functions of both isomers have significant contributions from at least two determinants, the first one being the hypothetical closed-shell configuration, and the second one being the double substitution of two electrons from the HOMO into the LUMO, meaning that the two frontier orbitals are strongly correlated. However, the coefficient of the second determinant is significantly higher in the case of the cyclopentanediyl **2SiH**₃-Me, resulting in a larger biradical character. The quantity $\beta = 2c_2^2/(c_1^2 + c_2^2)$ was proposed to estimate the biradical character^{1,62} and amounts to 24% for **2SiH**₃-Me, which compares nicely with similar singlet biradicals such as **2Ter**-R² (27%),⁴⁶ **1Ter** (27%),⁶³ or **1Hyp** (21%).³⁹ The biradical character of the cyclopentadiene **3SiH**₃-Me ($\beta = 10\%$) is significantly smaller and at the edge of what might still be regarded as a singlet biradical.^{62,64} (For example, benzene has been attributed 5–10% biradical character,^{65,66} in accordance with our own computations, cf. SI.)

Moreover, the CAS orbitals indicate that the HOMO of 3SiH₃-Me contributes to the P1-C1 and P2-N2 double-bond character (the LUMO being the corresponding antibonding orbital), whereas the HOMO of 2SiH₃-Me is mainly localized at the P atoms, forming a π -type antibond between the two P atoms (and thus describing the "radical sites" at P in conjunction with the partly occupied, transannularly bonding LUMO, cf. Figure 3). In line with these considerations, NRT⁶⁷ analyses of the DFT as well as CAS densities identified the diyl and diene Lewis resonance formulas as the most important contributions to 2SiH₃-Me and 3SiH₃-Me, respectively (Scheme 5). Note that in the NRT formalism, the "biradical" structures do not represent the multireference character of the wave function, though, but merely imply that the electrons in the HOMO are rather localized in a π -type antibond between the two P atoms. As such, it gives qualitative information about the localization of the radical sites but does not provide a measure of the biradical character!

Why, now, do we observe the formation of the biradical $2Hyp-R^2$ only in case of the Ter substituent, but formation of

Scheme 5. NRT Analyses of 2SiH₃-Me and 3SiH₃-Me⁴



" $R^1 = SiH_3$, $R^2 = Me$; PBE-D3/def2-SVP, delocalization threshold: 50 kcal/mol; please refer to the SI for the results using the CAS densities. Note that the "biradical" structures merely give information about the localization of the radical sites but not about the biradical character of the system!

the diene **3Hyp**-R² in all other cases? To investigate this matter, comprehensive computations covering all derivatives of **2Hyp**-R² and **3Hyp**-R² (R² = *t*Bu, Dmp, Mes, Ter) were performed (see SI for a complete set of structures). At the DLPNO-CCSD(T)⁶⁸⁻⁷⁰/def2-TZVP//PBE-D3/def2-SVP level of theory, it is apparent that the diene **3Hyp**-R² is the thermodynamically favored isomer for all substituents R² except Ter (Scheme 6). This is easily understood in terms of





large Pauli repulsion between the sterically demanding Hyp and Ter groups in the diene 3Hyp-R², where these two substituents are connected to the *same* N atom. In agreement with this consideration, the diene 3Hyp-tBu is also less stabilized than the derivatives 3Hyp-Dmp and 3Hyp-Mes, whose aromatic substituents have the smallest steric demand due to their rather flat structure (see the SI for buried volumes⁷¹ of all four substituents). Thus, the equilibrium between the diyl 2Hyp-R² and diene 3Hyp-R² formally depends on the steric demand of the substituent R².

Spectroscopic Properties. The different electronic structures of the derivatives of **2Hyp**-R² and **3Hyp**-R² could most easily be proven experimentally by UV–vis spectroscopy (cf. SI, p S30). While the biradical **2Hyp**-Ter showed broad absorption bands in the range of 500–680 nm (cf. **2Ter**-Dmp: $\lambda_{max} = 643$ nm), the dienes **3Hyp**-Dmp, **3Hyp**-Mes, and **3Hyp**-*t*Bu could be characterized by a single absorption maximum at 399–433 nm. This is in agreement with the calculated

biradical character (which depends, inter alia, on the HOMO– LUMO gap) and also corresponds to calculated values (TD-DFT PBE-D3/def2-TZVP, **2Hyp**-Ter 635 and 562, **3Hyp**-Dmp 494, **3Hyp**-Mes 494, **3Hyp**-*t*Bu 516 nm).

In the ³¹P NMR spectrum, diyl (**2Hyp**-R²) and diene (**3Hyp**-R²) are most readily distinguished by the J_{PP} coupling constant. Calculations for all isomers of **2Hyp**-R² and **3Hyp**-R² (R² = Dmp, Mes, tBu, Ter; cf. SI) predicted rather small coupling constants (10–17 Hz) for the dienes **3Hyp**-R², whereas the diyls **2Hyp**-R² were predicted to have substantially larger coupling constants (76–93 Hz). This could be verified experimentally: Only **2Hyp**-Ter displayed a large coupling constant of 118 Hz (calcd 93 Hz), while the other three species had small coupling constants of 10–15 Hz (calcd 10–13 Hz), in accordance with their diene character. While theory and experiment also agreed very nicely in case of the ³¹P NMR shifts, these were not suited to distinguish between diyl and diene, as they were quite similar for all species (Table 2).

Table 2. Experimental ³¹P NMR Data of 2Hyp-R² and 3Hyp-R^{2a}

		$\delta(P_A)$ [ppm]	$\delta(P_B)$ [ppm]	$J_{\rm PP}$ [Hz]
diyl	2Hyp-Dmp	- (211.8)	- (257.8)	- (79)
	2Hyp-Mes	- (213.6)	- (256.4)	- (79)
	2Hyp-tBu	- (176.5)	- (245.5)	- (76)
	2Hyp-Ter	211.7 (222.7)	275.1 (249.5)	118 (93)
diene	3Hyp-Dmp	209.0 (203.7)	297.3 (277.1)	15 (10)
	3Hyp-Mes	209.1 (204.4)	297.5 (278.0)	10 (10)
	3Hyp-tBu	230.7 (191.6)	281.9 (248.9)	15 (13)
	3Hyp-Ter	- (226.3)	- (253.6)	- (17)
^a Calculated data given in bra		in brackets (GIA	10 method, ^{72–76}	PBE-D3/
def2-SVP	P).			

Behavior under Irradiation. When a solution of the biradical **2Hyp**-Ter was irradiated with red light (638 nm), it photoisomerized to the corresponding housane-type species 2'Hyp-Ter (Scheme 7). In the ³¹P NMR spectrum, the

Scheme 7. While the Diyl 2Hyp-Ter (R^1 = Hyp) Could Be Photoisomerized to the Housane-Type Species 2'Hyp-Ter in Solution, the Same Is Not True of the Dienes 3Hyp-Dmp, 3Hyp-Mes, and 3Hyp-tBu



quantitative isomerization was evidenced by a large upfield shift of the two resonances to -128.1 and -69.2 ppm, respectively. In contrast, the dienes **3Hyp**-Dmp, **3Hyp**-Mes, and **3Hyp**-tBu could not be isomerized under irradiation, irrespective of the wavelength of the light (638, 520, and 445 nm). Even at -150 °C, we did not observe a change in the crystal structure when the samples were irradiated with white

light (in contrast to the previously published molecular switch **2Ter**-Dmp, whose crystals disintegrated under light due to isomerization to the housane **2'Ter**-Dmp).⁴⁶ Only in case of **3Hyp**-Mes, a B layer containing approximately 2% of the housane **3'Hyp**-Mes could be refined in the structural model, indicating either a very low quantum yield of the photo-isomerization or a very fast thermal reverse reaction even at very low temperatures.

The photoproduct 2'Hyp-Ter isomerized back to the biradical 2Hyp-Ter under thermal regime. The reaction could be traced by in situ ³¹P NMR spectroscopy at different temperatures (Figure 4). The kinetic data allowed us to



Figure 4. Thermal equilibration of the housane **2'Hyp**-Ter at 25 °C. For a full set of data at different temperatures, please refer to the SI, p. S36ff.

estimate the activation barrier of the reaction, which amounts to $\Delta G^{\ddagger} = 93 \pm 2 \text{ kJ/mol}$ at 25 °C (cf. SI). This compares to the activation barriers of thermal equilibration of the housanes **2'Ter**-Dmp (88 ± 4 kJ/mol) and **2'Ter**-tBu (ca. 94 kJ/mol).⁴⁶

Adduct Formation with a Second Equivalent of Isonitrile. The *t*Bu derivative 3Hyp-*t*Bu proved to be most difficult to isolate. While 3Hyp-Dmp and 3Hyp-Mes could be isolated in 70–90% yield, only a few crystals of 3Hyp-*t*Bu could be obtained. This was due to the formation of an adduct with a second equivalent of *t*BuNC (cf. Scheme 8), as evidenced by variable-temperature NMR spectroscopy. When 1Hyp was treated with 1 equiv of *t*BuNC at low temperatures,

Scheme 8. Trapping of the Biradical 2Hyp- R^2 ($R^1 = Hyp$) with a Second Equivalent of Isonitrile^{*a*}



"The adduct **4Hyp**-tBu could be detected spectroscopically. The hypothetical adduct **5Hyp**-R² is in gray.

exclusive formation of a new AX spin system (4Hyp-tBu) in a 1:1 ratio with the starting material was observed in the ³¹P NMR spectrum (Figure 5). Upon warming, the intensity of the



Figure 5. In situ 31 P NMR spectra of the reaction of 1Hyp with tBuNC at -40 and 25 °C. For spectra at additional temperatures, please see Figure S15.

new AX spin system decreased, while formation of yet another AX spin system was observed, which could be attributed to the diene **3Hyp**-*t*Bu. At ambient temperature, the diene **3Hyp**-*t*Bu was the main product, although traces of the starting material **1Hyp** as well as the intermediate **4Hyp**-*t*Bu were still present (10:1:3 ratio).

DFT and ab initio calculations indicated that the intermediate **4Hyp**-*t*Bu was in fact the *t*BuNC adduct of the transient biradical **2Hyp**-*t*Bu; that is, the unstable diyl **2Hyp**-*t*Bu could be trapped by adduct formation with *t*BuNC (Scheme 8; for calcd NMR data, please see Table S6). Upon warming, the adduct **4Hyp**-*t*Bu redissociated owing to the gain in entropy, and the transient biradical **2Hyp**-*t*Bu isomerized to the more stable diene **3Hyp**-*t*Bu. The hypothetical adduct **5Hyp**-*t*Bu was not observed (vide infra).

In case of the dienes **3Hyp**-Dmp and **3Hyp**-Mes, no adduct formation was observed. The same holds true for the stable diyl **2Hyp**-Ter. All these observations nicely agree with calculated thermodynamic data (DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP) for the reactions shown in Scheme 8. While reaction (i) is exergonic for all derivatives, reaction (ii), that is, the adduct formation step, is strongly exergonic solely in case of the *t*Bu derivative ($\Delta G^{\circ} = -40.5 \text{ kJ}/$ mol; cf. Table 3). As mentioned above, reaction (iii) is exergonic for R² = Dmp, Mes, and *t*Bu. The lowest energy gain is predicted for the *t*Bu derivative ($\Delta G^{\circ} = -29.5 \text{ kJ}/\text{mol}$), in line with the observed equilibrium between the adduct **4Hyp***t*Bu and the diene **3Hyp**-*t*Bu at ambient temperature. Reaction (iv), that is, the formation of the hypothetical isonitrile adduct

Table 3. Gibbs Free Energies ΔG° ($c^{\circ} = 1 \text{ mol/L}$, 298 K) for Reactions (i)–(iv) in kJ/mol (DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP, see also SI)^{*a*}

	reaction			
R ²	(i)	(ii)	(iii)	(iv)
Dmp	-63.5	-8.6	-62.1	+59.8
Mes	-58.8	-2.3	-62.7	+71.0
<i>t</i> Bu	-15.2	-40.5	-29.5	+52.2
Ter	-47.4	+168.4 ^b	+25.8	+137.6 ^b

^{*a*}Experimentally observed reaction pathways are printed in italics, and values printed in bold refer to those reactions whose products were detected experimentally. ^{*b*} ΔG° based on DLPNO-CCSD energy (the triples correction was not computed due to the size of the system).

5Hyp- R^2 , is strongly endergonic for all derivatives, and it was not observed. This is yet another indication for the low biradical character of the dienes **3Hyp**- R^2 .

CONCLUSION

In conclusion, we could demonstrate that the Hyp substituent introduced a new aspect into the chemistry of diphosphadiazanediyls (1R), namely the migration of a Hyp group depending on the stabilization and steric encumberment of the product species. Accordingly, treatment of 1Hyp with different isonitriles either led to the formation of a fivemembered biradical 2Hyp-Ter (in analogy to known 2Ter- R^2 derivatives) or afforded heterocyclopentadienes (3Hyp- R^2), which to the best of our knowledge represent the first isolated derivatives of 3H-1,3-diaza-2,4-diphosphole.

In our study, the diyl **2Hyp**-Ter displayed typical biradical reactivity, such as activation of small molecules or photoisomerization upon irradiation with visible light. In contrast, despite its similar molecular structure, the diene **3Hyp**-R² was rather unreactive, as it represented the thermodynamically favored isomer for smaller substituents at the isonitrile. Comprehensive computations were carried out to understand the differences in structure, bonding, and reactivity between both isomers, revealing that the biradical character of the diyl **2Hyp**-Ter is comparable to related compounds ($\beta = 24\%$), whereas the diene **3Hyp**-R² does not possess a significant biradical character ($\beta = 10\%$). Experimental techniques could be applied to verify the conclusions drawn from the theoretical models.

The isomerization of the diyl **2Hyp**-R² to the diene **3Hyp**-R² demonstrates that steric bulk alone is not necessarily sufficient to stabilize biradicals and that apparently small structural changes can lead to quite a different electronic situation. Consequently, these results will help us to devise new, stable singlet biradicals and molecular switches in the future.

EXPERIMENTAL SECTION

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk or Drybox techniques.

Solvents were obtained from commercial sources. CH_2Cl_2 was purified according to a literature procedure,⁷⁷ dried over P_4O_{10} , and stored over CaH_2 and was freshly distilled and degassed (by at least three freeze–pump–thaw cycles) prior to use. *n*-Hexane was dried over Na/benzophenone/tetraglyme. CD_2Cl_2 was dried over P_4O_{10} and stored over CaH_2 . C_6D_6 was dried over Na. THF- d_8 was dried over Na and stored over molecular sieves (4 Å) after distillation. All solvents were freshly distilled prior to use.

Reactants and starting materials were either purchased or synthesized according to literature procedures. NEt₃ (Sigma-Aldrich, 99%) was dried over Na and distilled. Mg turnings (abcr, 99.8%, for Grignards) were activated by stirring for several days under argon atmosphere using a glass-coated magnetic stir bar. POCl₃ (old stock) was dried over P₄O₁₀, distilled and degassed. DmpNH₂ (Acros, 99%) was distilled. [NEt₄]Br (Fluka, 98%), [PhNEt₃]Br (Sigma-Aldrich, 98%), and NaOH (Grüssing, 99%) were used as received. TerNH₂^{78,79} and [CIP(μ -NHyp)]₂⁸⁰ were synthesized according to literature procedures.

NMR Spectra. Spectra were obtained on Bruker spectrometers AVANCE 250, 300, or 500 and were referenced internally to the signals of deuterated solvents (¹³C: CD₂Cl₂ δ_{ref} = 54.0 ppm, C₆D₆ δ_{ref} = 128.4 ppm, THF- $d_8 \delta_{ref,1}$ = 25.4 ppm, $\delta_{ref,2}$ = 67.6 ppm), to the signals of protic species in the deuterated solvents (¹H: CHDCl₂ δ_{ref} = 5.32 ppm, C₆HD₅ δ_{ref} = 7.16 ppm, THF- $d_7 \delta_{ref,1}$ = 1.73 ppm, $\delta_{ref,2}$ =

3.58 ppm), or externally (³¹P: 85% H₃PO₄ $\delta_{ref} = 0$ ppm). All measurements were carried out at ambient temperature (25 °C) unless denoted otherwise. NMR signals were assigned using experimental data (e.g., chemical shifts, coupling constants, integrals where applicable) in conjunction with computed NMR data (GIAO method, cf. Computational Details).

NMR Spectra under Irradiation. Spectra were recorded by means of an adopted setup previously published by the Gschwind group,⁸¹ who used a fiber-coupled light emitting diode (LED) to direct light into the NMR spectrometer. Instead of LEDs, a laser diode (Oclaro HL63193MG, 638 nm, 700 mW) was used. To ensure inert conditions, all samples were prepared in a glovebox, and the tubes were sealed with custom-made PTFE caps as well as 2–3 layers of PTFE tape.⁴⁶

IR Spectra. Spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer equipped with a Smart Orbit ATR unit or a Bruker Alpha II FT-IR spectrometer with an ATR unit at ambient temperature (25 $^{\circ}$ C).

Raman Spectra. Spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red laser (633 nm, 17 mW, air-cooled HeNe laser) or blue laser (473 nm, 20 mW, air-cooled solid-state laser). All measurements were carried out at ambient temperature (25 $^{\circ}$ C) unless stated otherwise.

Elemental Analyses. Results were obtained using an Elementar vario Micro cube CHNS analyzer or a LECO TruSpec Micro CHNS analyzer.

Melting Points. Results (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min.

Mass Spectra. Spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples.

UV-vis Spectra. Spectra were acquired on a PerkinElmer Lambda 19 UV-vis spectrometer.

X-ray Structure Determination. Single crystals of **3Hyp-**Dmp, **3Hyp-**Mes, and **3Hyp**-*t*Bu were obtained by crystallization from *n*-hexane at -40 °C. X-ray quality crystals were selected in Fomblin YR-1800 perfluoro-ether (Alfa Aesar) at ambient temperature (25 °C). The samples were cooled to 123(2) K or 298(2) K during measurements. The data were collected on a Bruker D8 Quest diffractometer or a Bruker Kappa Apex II diffractometer using Mo K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by iterative methods (SHELXT)⁸² and refined by full matrix least-squares procedures (SHELXL).⁸³ Semiempirical absorption corrections were applied (SADABS).⁸⁴ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions using a riding model.

Computational Details. Computations were carried out using Gaussian 09⁸⁵ or ORCA 4.1.1⁸⁶ and the standalone version of NBO 6.0.^{87–92} Structure optimizations were performed using the pure DFT functional PBE^{50,51} in conjunction with Grimme's dispersion correction D3(BJ)^{93,94} and the def2-SVP basis set⁵² (notation PBE-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. The validity of the single-determinantal Kohn–Sham DFT approach was verified by stability analyses of the KS wave functions. Chemical shifts and coupling constants were derived by the GIAO method.^{72–76} The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85% H₃PO₄ in the gas phase ($\sigma_{ref,1} = 328.35$ ppm),⁹⁵ using PH₃ ($\sigma_{ref,2} = 594.45$ ppm) as a secondary standard:⁹⁶

$$\delta_{\text{calc},X} = (\sigma_{\text{ref},1} - \sigma_{\text{ref},2}) - (\sigma_{\text{calc},X} - \sigma_{\text{calc},PH_3})$$
$$= \sigma_{\text{calc},PH_3} - \sigma_{\text{calc},X} - 266.1 \text{ ppm}$$

At the PBE-D3/def2-SVP level of theory, $\sigma_{\rm calc,PH_3}$ amounts to +617.15 ppm. Thermal corrections to the total energy were computed at the PBE-D3/def2-SVP level of theory. More accurate estimates of the electronic energy were obtained by single-point DLPNO-CCSD(T)/ def2-TZVP or DLPNO-CCSD/def2-TZVP^{68-70} computations (nota-

tion DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP or DLPNO-CCSD/def2-TZVP//PBE-D3/def2-SVP). The T_1 diagnostic was evaluated in each case to ensure reliable results. (Empirically, CCSD(T) results with T_1 values smaller than 0.02 are considered reliable.)¹³ To investigate the electronic structures of the diyls **2Hyp** and dienes **3Hyp** in more detail, the model systems **2SiH**₃-Me and **3SiH**₃-Me were used. CASSCF(8,6)/def2-TZVP⁵³⁻⁶¹ computations including all π -type electrons in the active space were performed to investigate the biradical character. NRT analyses⁶⁷ of the DFT and CAS densities were computed to localize the electrons and obtain Lewis-type descriptions of the bonding patterns. It should be emphasized that all computations were carried out for single, isolated gas phase molecules. There may be significant differences between gas phase, solution, and solid state.

Syntheses. DmpNC. DmpNC was synthesized according to a modified literature procedure.³⁴ The synthesis was carried out under non-inert conditions. In a three-necked flask equipped with a reflux condenser and a dropping funnel, DmpNH₂ (3.36 g, 29.7 mmol), chloroform (3.55 g, 29.7 mmol), and [NEt₄]Br (90 mg, 0.43 mmol) are dissolved in CH₂Cl₂ (30 mL). Under vigorous stirring, a solution of NaOH (30 g, 0.75 mol) in water (30 mL) is added slowly over a period of 15 min. The mixture is stirred for 18 h without an external heat source, but with the reflux condenser turned on as to prevent evaporation of the organic solvents due to the exothermic reaction. Afterward, the reaction mixture is diluted with water (200 mL). The aqueous phase is extracted three times with CH_2Cl_2 (50 mL). The solvents of the combined organic phases are evaporated, and the solid residue is sublimed three times (1×10^{-3} mbar, 70 °C, oil bath). A final sublimation at ambient temperature $(1 \times 10^{-3} \text{ mbar, } 25 \text{ }^{\circ}\text{C})$ yields colorless crystals of the product (yield: 2.05 g, 15.6 mmol, 53%). C₉H₉N (131.18 g/mol). Mp. 77 °C. Anal. calcd for C₉H₉N: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.75; H, 6.44; N, 10.90. ¹H NMR (CD₂Cl₂, 300.1 MHz): δ 2.41 (s, 6H), 7.12 (d, 1H, J = 8 Hz), 7.19 (t, 2H, J = 7 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 19.1, 128.1, 129.0, 135.3, 168.7. IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu}$ = 3233 (w), 3184 (w), 2984 (w), 2947 (w), 2920 (w), 2881 (w), 2739 (w), 2120 (m), 2085 (w), 1949 (w), 1879 (w), 1811 (w), 1655 (m), 1591 (w), 1525 (w), 1490 (w), 1471 (m), 1440 (m), 1379 (m), 1302 (w), 1282 (w), 1228 (w), 1170 (m), 1084 (m), 1036 (m), 991 (w), 977 (w), 923 (w), 800 (w), 775 (vs), 721 (m), 637 (w), 548 (w). Raman (633 nm, 20 s, 20 scans, cm⁻¹): $\tilde{\nu} = 3071$ (3), 3043 (3), 2985 (3), 2947 (4), 2919 (10), 2911 (9), 2885 (3), 2882 (3), 2873 (3), 2863 (4), 2740 (3), 2735 (3), 2119 (7), 1600 (1), 1590 (2), 1471 (1), 1464 (1), 1437 (1), 1423 (1), 1408 (1), 1383 (1), 1373 (1), 1264 (1), 1254 (2), 1171 (2), 1092 (1), 1078 (2), 990 (1), 796 (1), 779 (1), 727 (1), 719 (1), 636 (8), 565 (1), 542 (1), 518 (1), 505 (1), 491 (1), 458 (1), 361 (4), 284 (1), 240 (2). MS (GC-MS) m/z (%): 103 $(30) [C_7H_4N]^+, 116 (62) [C_8H_8N]^+, 130 (100) [C_9H_8N]^+, 131 (68)$ [M]+.

MesNC. MesNC was synthesized according to a modified literature procedure.³⁴ The synthesis was carried out under non-inert conditions. In a three-necked flask equipped with a reflux condenser and a dropping funnel, $MesNH_2$ (4.39 g, 32.4 mmol), chloroform (3.85 g, 33.0 mmol), and [PhNEt₃]Cl (0.18 mg, 0.8 mmol) are dissolved in CH₂Cl₂ (50 mL). Under vigorous stirring, a solution of NaOH (30 g, 0.75 mol) in water (30 mL) is added slowly over a period of 15 min. The mixture is stirred for 22 h without external heat source, but with the reflux condenser turned on as to prevent evaporation of the organic solvents due to the exothermic reaction. Afterward, the reaction mixture is diluted with water (200 mL). The aqueous phase is extracted three times with CH₂Cl₂ (50 mL). The solvents of the combined organic phases are evaporated, and the solid residue is sublimed $(1 \times 10^{-3} \text{ mbar}, 60-70 \text{ °C}, \text{ oil bath})$. The product was then crystallized from dry $\mathrm{CH_2Cl_2}$ (yield: 2.50 g, 17.22 mmol, 53%). C₁₀H₁₁N (145.20 g/mol). Mp. 42 °C. Anal. calcd for C₁₀H₁₁N: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.47; H, 7.51; N, 9.77. ¹H NMR (CD₂Cl₂, 250.1 MHz): δ 2.29 (s, 6H), 2.36 (s, 3H), 6.92 (s, 2H). ¹³C{¹H} NMR (CD₂Cl₂, 250.1 MHz): δ 18.9, 21.2, 128.7, 129.0, 134.9, 139.3, 168.0. IR (ATR, 25 °C, 32 scans, cm⁻¹): $\tilde{\nu} = 3031$ (w), 2976 (w), 2947 (w), 2916 (w), 2854 (w), 2739 (w), 2256 (w),

2116 (vs), 2083 (w), 1935 (w), 1902 (w), 1789 (w), 1754 (w), 1605 (m), 1556 (w), 1477 (m), 1445 (m), 1434 (m), 1377 (m), 1311 (w), 1284 (w), 1255 (w), 1199 (m), 1146 (w), 1127 (w), 1039 (m), 1020 (w), 956 (w), 944 (w), 931 (w), 896 (w), 859 (s), 816 (w), 719 (m), 707 (w), 666 (w), 598 (w), 573 (m), 503 (w), 422 (w), Raman (473 nm, 4 s, 20 scans, cm⁻¹): $\tilde{\nu} = 3033$ (1), 3021 (1), 2976 (1), 2922 (2), 2861 (1), 2737 (1), 2114 (10), 2080 (1), 1606 (3), 1476 (1), 1438 (1), 1418 (1), 1386 (1), 1307 (2), 1196 (1), 1143 (1), 1124 (1), 953 (1), 703 (1), 595 (1), 576 (2), 499 (1), 422 (1), 283 (1). MS (GC-MS) m/z (%): 103 (17) $[C_7H_5N]^+$, 115 (12) $[C_8H_5N]^+$, 130 (100) $[C_9H_8N]^+$, 145 (50) $[M]^+$.

TerN(H)CHO. Terphenyl formamide was synthesized according to a modified literature procedure.⁹⁷ The synthesis was carried out under non-inert conditions. TerNH₂ (1.698 g, 5.150 mmol), ZnCl₂ (0.627 g, 4.601 mmol), and formic acid (4.063 g, 88.27) are stored for 86 h at 60 °C (drying oven). The crystals are washed two times with water, and the aqueous phase is discarded. The product is dissolved in CH₂Cl₂ (20 mL) and separated from impurities and water residues in a separating funnel. The organic solvent is evaporated, and the solid is dried in vacuo (1 \times 10⁻³ mbar). Yield: 1.320 g, 4.001 mmol, 80%. C₂₅H₂₇NO (357.50 g/mol). Mp. 305 °C. Anal. calcd for C₂₅H₂₇NO: C, 83.69; H, 7.61; N, 3.92. Found: C, 83.40; H, 7.66; N, 3.82. ¹H NMR (CD₂Cl₂, 250.1 MHz): δ 2.01 (s, 12H), 2.32 (s, 6H), 6.47 (br s, 1H), 6.98 (s, 4H), 7.13 (d, 2H, J = 7.4 Hz), 7.35 (t, 1H, J = 7.4 Hz), 7.58 (d, 1H, I = 10 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 62.9 MHz): δ 20.7, 21.4, 126.6, 128.5, 128.9, 129.2, 130.8, 132.9, 134.4, 135.3, 136.4, 138.3, 162.6. IR (ATR, 25 °C, 32 scans, cm⁻¹): $\tilde{\nu} = 3358$ (w), 2972 (w), 2937 (w), 2912 (m), 2855 (w), 2733 (w), 1678 (s), 1612 (m), 1455 (m), 1408 (m), 1377 (m), 1272 (s), 1239 (s), 1206 (m), 1177 (m), 1101 (m), 1070 (m), 1033 (m), 1012 (m), 983 (m), 888 (m), 857 (s), 812 (s), 765 (m), 742 (m), 688 (m), 629 (m), 585 (m), 575 (m), 552 (m), 507 (m), 453 (m). Raman (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu} = 3360$ (1), 3056 (1), 3023 (2), 2973 (2), 2915 (6), 2855 (2), 2735 (1), 1685 (2), 1613 (5), 1588 (2), 1575 (2), 1486 (2), 1458 (2), 1384 (4), 1308 (9), 1208 (1), 1168 (2), 1072 (2), 1009 (3), 947 (2), 889 (2), 743 (1), 690 (1), 577 (10), 563 (5), 522 (5), 456 (2), 374 (2), 327 (2), 269 (3), 244 (3).

TerNC. Terphenyl isonitrile was synthesized according to a modified literature procedure.⁹⁷ To a solution of terphenyl formamide (0.603 g, 1.687 mmol) in CH₂Cl₂ (13 mL), NEt₃ (1.697 g, 16.77 mmol) is added at 0 °C. Under stirring and cooling, POCl₃ (0.680 g, 4.44 mmol) is added slowly. The orange solution is stirred for 16 h at ambient temperature (25 °C). Afterward, the reaction mixture is quenched with water at 0 °C. The organic phase is extracted two times with water (20 mL) and three times with saturated aqueous NaHCO₃ (20 mL). The pale yellow organic layer is separated, dried over MgSO₄, and filtered. The organic solvent is removed under reduced pressure (1×10^{-3} mbar). The raw product is washed three times with *n*-hexane, and the colorless crystals are dried in vacuo (1 \times 10^{-3} mbar). Yield: 0.231 g, 0.680 mmol, 40%. $C_{25}H_{25}N$ (339.48 g/ mol). Mp. 266 °C. Anal. calcd for C25H25N: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.64; H, 7.48; N, 3.90. ¹H NMR (CD₂Cl₂, 300.1 MHz): δ 2.02 (s, 12H), 2.34 (s, 6H), 7.00 (s, 4H), 7.22 (d, 2H, J = 7.7 Hz), 7.54 (t, 1H, I = 7.7 Hz) ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 75.5 MHz): δ 20.4, 21.4, 128.8, 130.0, 130.1, 134.9, 136.2, 138.4, 139.8, 185.4. IR (ATR, 25 °C, 32 scans, cm⁻¹): $\tilde{\nu} = 2999$ (w), 2974 (w), 2943 (w), 2914 (m), 2853 (w), 2733 (w), 2624 (w), 2605 (w), 2496 (w), 2119 (m), 1614 (m), 1573 (w), 1455 (m), 1416 (m), 1377 (m), 1274 (w), 1183 (w), 1068 (w), 1035 (m), 1014 (m), 981 (w), 919 (w), 862 (m), 851 (m), 806 (s), 787 (m), 759 (s), 738 (m), 608 (m), 575 (m), 565 (m), 519 (m), 497 (m). Raman (633 nm, 10 s, 10 scans, cm⁻¹): $\tilde{\nu} = 3069$ (1), 3058 (1), 3012 (1), 2918 (1), 2857 (1), 2734 (1), 2121 (10), 2087 (1), 1614 (1), 1584 (1), 1490 (1), 1416 (1), 1381 (1), 1308 (4), 1288 (1), 1273 (1), 1188 (2), 1184 (2), 1161 (1), 1067 (3), 1000 (1), 947 (1), 612 (2), 579 (4), 564 (1), 524 (1), 499 (1), 406 (1), 380 (1), 336 (1), 255 (1), 233 (1).

 $[P(\mu-NHyp)]_2$ (**1Hyp**). $[PCl(\mu-NHyp)]_2$ was synthesized according to a modified literature procedure.³⁹ $[ClP(\mu-NHyp)]_2$ (1.912 g, 2.913 mmol) and Mg turnings (0.725 g, 26.8 mmol) are combined in a Schlenk flask. It is paramount to ensure that no grease finds its way into

the reaction vessel, as this may deactivate the Mg turnings. DME is added (50 mL), and the reaction mixture is stirred at ambient temperature (25 °C). The colorless mixture gradually turns dark red. The progress of the reaction must by monitored by ³¹P NMR spectroscopy, as overreduction and dimerization of the product occur very quickly. When the reaction is completed, the solvent is removed in vacuo (1×10^{-1}) mbar), and the solids are dried at 50 °C (oil bath) for 30 min. n-Hexane (15 mL) is added, and the insoluble material is separated by filtration. If necessary, the cloudy suspension is filtered a second time over a Celite-padded frit. The product is crystallized from a minimal amount of *n*-hexane at -40 °C. After crystallization overnight, red crystals of the product are obtained. The supernatant is removed by syringe, concentrated, and stored at -40 °C, yielding a second crop of product. The isolated crystals are dried in vacuo (1×10^{-3} mbar). Yield: 1.338 g, 2.286 mmol, 70%. C₁₈H₅₄N₂P₂Si₈ (585.27 g/mol). Mp. 205 °C. Anal. calcd for C₁₈H₅₄N₂P₂Si₈: C, 36.94; H, 9.30; N, 4.79. Found: C, 36.59; H, 9.34; N, 4.72. ¹H NMR (C₆D₆, 300.1 MHz): δ 0.21 (s, 54H). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 125.5 MHz): δ 1.13. ${}^{14}N$ NMR: No signals observed. ²⁹Si-INEPT NMR (C_6D_6 , 59.6 MHz): δ –13.02 (m, 6Si), -35.02 (m, 2Si). ³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ 320.4 (quin, 2P, J = 44 Hz). IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu} = 2949$ (w), 2893 (w), 2818 (w), 2794 (w), 2652 (w), 2368 (w), 2326 (w), 2085 (w), 2050 (w), 1984 (w), 1927 (w), 1863 (w), 1595 (w), 1495 (w), 1439 (w), 1396 (w), 1240 (m), 1053 (w), 982 (w), 947 (w), 816 (vs), 789 (s), 760 (s), 750 (s), 681 (s), 623 (s), 559 (m). Raman (633 nm, 10 s, 10 scans, cm⁻¹): $\tilde{\nu} = 2949$ (5), 2927 (3), 2890 (10), 1396 (1), 1259 (1), 1240 (1), 1138 (1), 1116 (1), 1070 (2), 865 (1), 834 (1), 802 (1), 744 (1), 686 (3), 625 (7), 587 (1), 464 (1), 431 (1), 370 (1), 304 (2), 263 (1), 215 (2), 178 (8), 173 (8), 164 (9), 161 (9). MS (CI pos., isobutane), m/z (%): 247 (1) [Si(Si- $(CH_3)_3)_3]^+$, 264 (2) $[Si(Si(CH_3)_3)_3NH_3]^+$, 292 (2) $[Si(Si-1)_3)_3NH_3]^+$, 292 (2) $[Si(Si-1)_3]_3NH_3]^+$, 292 (2) [Si(Si-1)_3]_3NH_3]^+, 292 (2) [Si(Si-1)_3]_3NH_3]^+, 292 (2) [Si(Si-1)_3]_3NH_3]^+, 292 (2) [Si(Si-1)_3]_3NH_3]_3NH_3]^+, 292 (2) [Si(Si-1)_3NH_3]_3NH_3]^+, 292 ($(CH_3)_3)_3NP$ ⁺, 555 (2) $[Si_2(Si(CH_3)_3)_6NP]^+$, 584 (100) $[M]^+$, 585 $(67) [M + H]^+$

3Hyp-Dmp. To a solution of $[P(\mu-NHyp)]_2$ (**1Hyp**; 274 mg, 0.470 mmol) in hexane (5 mL), DmpNC (60 mg, 0.47 mmol) is added. An immediate color change from orange to green to yellow is observed. After 2 h, the solvent is removed, and the yellow residue is dried in vacuo (1 \times 10⁻³ mbar). The product is crystallized from a minimal amount of fresh *n*-hexane at -40 °C. The supernatant is removed by syringe, and the crystals are dried in vacuo (1 \times 10⁻³ mbar). Yield: 230 mg, 0.32 mmol, 68%. $C_{27}H_{63}N_3P_2Si_8$ (715.45 g/mol). Mp. 205 °C. Anal. calcd for C₂₇H₆₃N₃P₂Si₈: C, 45.26; H, 8.86; N, 5.87. Found: C, 45.36; H, 9.04; N, 5.70. ¹H NMR (C_6D_6 , 300.1 MHz): δ 0.21 (s, 27H), 0.33 (s, 27H), 2.39 (s, 6H), 6.94 (s, 3H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR $(C_6D_{6}, 75.5 \text{ MHz})$: $\delta 0.0, 1.9, 18.6 \text{ (d, } J = 3 \text{ Hz}), 127.2, 129.3, 136.0$ (d, J = 3 Hz), 144.7 (d, J = 4 Hz). ¹⁴N NMR: No signals observed. ²⁹Si-INEPT NMR (C_6D_6 , 59.6 MHz): δ -13.2 (m, 3Si), -14.3 (m, 3Si), -30.8 (m, 1Si), -33.8 (m, 1Si). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 121.5 MHz): δ = 209.0 (d, 1P, J = 15 Hz, CPN), 297.3 (d, 1P, J = 15 Hz, NPN). IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu} = 2949$ (w), 2893 (w), 1599 (w), 1589 (w), 1539 (m), 1470 (w), 144 (w), 1398 (w), 1325 (w), 1242 (m), 1203 (m), 1194 (m), 1097 (w), 99 (m), 937 (m), 910 (m), 825 (vs), 791 (s), 744 (m), 685 (s), 621 (m), 553 (m), 540 (m). Raman (633 nm, 20 s, 20 scans, cm⁻¹): $\tilde{\nu} = 3068$ (1), 3036 (1), 3017 (1), 2952 (3), 2895 (7), 1594 (1), 1467 (1), 1441 (1), 1406 (1), 1380 (1), 1335 (2), 1332 (2), 1263 (2), 1241 (2), 1222 (1), 1197 (10), 1164 (1), 1101 (1), 1032 (1), 1017 (4), 913 (3), 894 (1), 890 (1), 862 (1), 828 (2), 794 (4), 780 (1), 748 (2), 738 (1), 726 (1), 713 (3), 690 (3), 632 (9), 623 (5), 556 (5), 544 (3), 530 (2), 490 (1), 472 (1), 455 (1), 440 (2), 415 (4), 397 (1), 375 (1), 348 (1), 320 (3), 295 (2), 272 (2), 253 (2), 241 (2), 221 (3), 176 (7), 127 (3), 81 (6). MS (CI pos., isobutane), *m/z* (%): 424 (18) [DmpNHypCNP]⁺, 497 (26) [DmpNHypCN₂P₂Si]⁺, 645 (4) $[DmpNHypCN_2P_2SiSi_2(CH_3)_3]^+$, 700 (21) $[C_7H_6N_3P_2CHyp_2]^+$, 701 (14) $[C_7H_7N_3P_2CHyp_2]^+$, 702 (10) $[C_7H_8N_3P_2CHyp_2]^+$, 715 (100) $[M]^+$, 716 (86) $[M + H]^+$. Single crystals suitable for X-ray structure determination can be obtained by recrystallization from fresh *n*-hexane at -40 °C.

3Hyp-Mes. To a solution of $[P(\mu-NHyp)]_2$ (**1Hyp**; 271 mg, 0.464 mmol) in hexane (8 mL), MesNC (66 mg, 0.46 mmol) is added. An

immediate color change from orange to green to yellow is observed. After 2 h, the solvent is removed, and the yellow residue is dried in vacuo (1 \times 10⁻³ mbar). The product is crystallized from a minimal amount of fresh *n*-hexane at -40 °C. The supernatant is removed by syringe, and the crystals are dried in vacuo (1 \times 10⁻³ mbar). Yield: 315 mg, 0.43 mmol, 93%. C28H65N3P2Si8 (730.48 g/mol). Mp. 207 °C. Anal. calcd for C₂₈H₆₅N₃P₂Si₈: C, 46.04; H, 8.97; N, 5.75. Found: C, 46.01; H, 9.09; N, 5.50. ¹H NMR (CD₂Cl₂, 300.1 MHz): δ 0.13 (s, 27H), 0.21 (s, 27H), 2.18 (s, 6H), 2.29 (s, 3H), 6.91 (s, 2H). ¹³C{¹H} NMR (C₆D₆, 75.5 MHz): δ 0.0, 1.9, 18.5 (d, *J* = 3 Hz), 20.2, 127.2, 130.1, 135.5 (d, J = 4 Hz), 136.5. ¹⁴N NMR: No signals observed. ²⁹Si-INEPT NMR (C₆D₆, 59.6 MHz): δ –13.2 (m, 3Si), -14.4 (m, 3Si), -31.0 (m, 1Si), -33.6 (m, 1Si). ${}^{31}P{}^{1}H$ NMR (C₆D₆, 121.5 MHz): $\delta = 209.1$ (d, 1P, CPN, ${}^{2}J{}^{(31}P{}^{31}P) = 10$ Hz), 297.5 (d, 1P, NPN, ${}^{2}J({}^{31}P, {}^{31}P) = 10$ Hz). IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu}$ = 2949 (w), 2891 (w), 1529 (w), 1477 (w), 1439 (w), 1396 (w), 1333 (m), 1304 (w), 1259 (m), 1240 (m), 1200 (m), 1188 (w), 1157 (w), 1034 (w), 1012 (w), 984 (w), 957 (w), 930 (w), 908 (w), 825 (vs), 771 (m), 744 (m), 710 (m), 683 (m), 621 (m), 567 (m), 528 (m). Raman (633 nm, 10 s, 20 scans, cm⁻¹): $\tilde{\nu} = 3010$ (1), 2974 (2), 2952 (3), 2930 (2), 2894 (8), 2824 (1), 2779 (1), 2734 (0), 1610 (1), 1573 (0), 1484 (0), 1443 (0), 1407 (0), 1382 (1), 1374 (1), 1332 (1), 1304 (1), 1263 (1), 1244 (1), 1200 (4), 1188 (4), 1158 (0), 1015 (2), 957 (0), 908 (2), 859 (1), 823 (1), 774 (2), 747 (1), 736 (0), 712 (1), 690 (2), 633 (10), 579 (2), 570 (1), 568 (1), 549 (4), 530 (2), 504 (0), 454 (1), 445 (1), 425 (2), 401 (1), 366 (2), 327 (1), 301 (1), 240 (1), 220 (1), 177 (6), 133 (2), 102 (2). MS (CI pos., isobutane); m/z (%): 350 (1) [HypN₂P₂C]⁺, 482 (1) $[HypN_3P_2CMes]^+$, 583 (1) $[HypN_3P_2CSi_2(CH_3)_3]^+$, 656 (28) $[HypN_3P_2CSi_3(CH_3)_6]^+$, 714 (28) $[Hyp_2N_3P_2CC_8H_8]^+$, 715 (19) $[Hyp_2N_3P_2CC_8H_9]^+$, 716 (13) $[Hyp_2N_3P_2CC_8H_{10}]^+$, 729 (100) $[M]^+$, 730 (83) $[M + H]^+$. Single crystals suitable for X-ray structure determination can be obtained by recrystallization from fresh nhexane at -40 °C.

3Hyp-tBu. To a solution of $[P(\mu-NHyp)]_2$ (**1Hyp**; 305 mg, 0.521 mmol) in hexane (5 mL), 'BuNC (58 μL, 43 mg, 0,521 mmol) is added via microliter syringe. An immediate color change from orange to blue to green to yellow is observed. After 2 h, all volatiles are removed, and the yellow residue is dried in vacuo (1×10^{-3} mbar). The product is crystallized from a minimal amount of fresh *n*-hexane at -40 °C. Only a few crystals can be obtained due to the equilibrium chemistry described above. $C_{23}H_{63}N_3P_2Si_8$ (668.40 g/mol). ¹H NMR (CD_5CD_3 , 300.1 MHz): δ 0.24 (s, 27H), 0.27 (s, 27H), 1.48 (s, 9H). ³¹P{¹H} NMR ($C_6D_5CD_3$, 121.5 MHz): δ 230.7 (d, 1P, *J* = 15 Hz, CPN), 281.9 (d, 1P, *J* = 15 Hz, NPN). Single crystals suitable for X-ray structure determination can be obtained by recrystallization from fresh *n*-hexane at -40 °C. Due to the dynamic equilibrium chemistry, no further analysis of the pure species was possible.

4Hyp-tBu. To a solution of $[P(\mu-NHyp)]_2$ (**1Hyp**; 301 mg, 0.520 mmol) in hexane (5 mL), 'BuNC (0.58 mL, 430 mg, 5.212 mmol) is added via microliter syringe. An immediate color change from orange to blue to green to yellow is observed. After 2 h, the solvent and excess 'BuNC are removed, and the yellow residue is dried in vacuo $(1 \times 10^{-3} \text{ mbar})$. A mixture of several species is obtained, with the main components being **3Hyp**-tBu and **4Hyp**-tBu in a 2:5 ratio. $C_{28}H_{72}N_4P_2Si_8$ (751.58 g/mol). ¹H NMR ($C_6D_5CD_3$, 300.1 MHz): diene **3Hyp**-tBu: δ 0.29 (s, 27H), 0.30 (s, 27H), 1.45 (s, 9H); adduct **4Hyp**-tBu: δ 0.31 (s, 27H), 0.39 (s, 27H), 1.48 (s, 9H). ³¹P{¹H} NMR ($C_6D_5CD_3$, 121.5 MHz): diene **3Hyp**-tBu: δ 230.7 (d, 1P, *J* = 15 Hz, CPN), 281.9 (d, 1P, *J* = 15 Hz, NPN); adduct **4Hyp**-tBu: δ 177.7 (d, 1P, *J* = 22 Hz, NPN), 233.1 (d, 1P, *J* = 22 Hz, NPN). Separation of the products and further analysis of the pure species was not possible.

2Hyp-Ter. To a solution of $[P(\mu-NHyp)]_2$ (**1Hyp**; 139 mg, 0.236 mmol) in hexane (6 mL), TerNC (80 mg, 0.24 mmol) is added. An immediate color change from orange to blue is observed. After 2 h, the solvent is removed, and the blue residue is dried in vacuo (1 × 10^{-3} mbar). Due to the product's high sensitivity, some byproducts are obtained that prevented recrystallization, and the sample was used for further experiments. C₄₃H₇₉N₃P₂Si₈ (925.75 g/mol). ¹H NMR

(C₆D₆, 500.1 MHz): δ 0.15 (s, 27H), 0.26 (s, 27H), 2.22 (s, 6H), 2.29 (s, 6H), 2.52 (s, 6H), 6.82 (m, 4H), 7.04 (s, 3H). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 1.1, 1.9 (d, *J* = 3 Hz), 21.3, 23.2, 27.4, 123.4, 129.1, 129.4, 130.9, 132.5, 135.5, 136.3, 137.3, 137.6, 139.8, 155.6. ¹⁴N NMR: No signals observed. ²⁹Si-INEPT NMR (C₆D₆, 99.4 MHz): δ -11.9 (m, 3Si), -12.8 (m, 3Si), -26.2 (m, 1Si), -42.4 (m, 1Si). ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 211.7 (br d, 1P, *J* = 118 Hz, CPN), 275.1 (br d, 1P, *J* = 118 Hz, NPN). The product was highly labile. Therefore, isolation and further analysis of the pure species were not possible.

Irradiation of 2Hyp-Ter. **1Hyp** (25.8 mg, 0.043 mmol) and TerNC (17.8 mg, 0.043 mmol) are dissolved in THF- d_8 (0.45 mL). The blue solution was irradiated in the NMR spectrometer with red light (638 nm). After full conversion to the housane **2'Hyp-**Ter, the light source was shut off, and the thermal reverse reaction was traced by ³¹P NMR spectroscopy. ³¹P{¹H} NMR of **2'Hyp-**Ter (THF- d_8 , 101 MHz): δ –128.0 (d, 1P, J = 91 Hz, NPC), –69.0 (d, 1P, J = 91 Hz, NPN).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c00460.

Crystal structure of 3Hyp-Dmp (CIF)

Crystal structure of 3Hyp-Mes (CIF)

Crystal structure of 3Hyp-*t*Bu (CIF)

Experimental and computational details, spectroscopic data including copies of experimental spectra, further information on irradiation experiments and kinetic studies. CCDC 1983541–1983543 contain the supplementary crystallographic data for this paper (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Jonas Bresien Institute of Chemistry, University of Rostock, 18059 Rostock, Germany; o orcid.org/0000-0001-9450-3407; Email: jonas.bresien@uni-rostock.de
- Axel Schulz Institute of Chemistry and Department Life, Light, and Matter, University of Rostock, 18059 Rostock, Germany; Leibniz Institute for Catalysis, 18059 Rostock, Germany;
 orcid.org/0000-0001-9060-7065; Email: axel.schulz@unirostock.de

Authors

- Henrik Beer Institute of Chemistry, University of Rostock, 18059 Rostock, Germany
- Dirk Michalik Institute of Chemistry, University of Rostock, 18059 Rostock, Germany; Leibniz Institute for Catalysis, 18059 Rostock, Germany
- Anne-Kristin Rölke Institute of Chemistry, University of Rostock, 18059 Rostock, Germany
- Alexander Villinger Institute of Chemistry, University of Rostock, 18059 Rostock, Germany; Orcid.org/0000-0002-0868-9987
- Ronald Wustrack Institute of Chemistry, University of Rostock, 18059 Rostock, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c00460

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are indebted to the ITMZ of the University of Rostock for access to the high-performance computing facilities. Especially, we wish to thank Malte Willert for his continuous support with all software-related issues. Furthermore, we wish to thank the DFG (SCHU/1170/12-2) for financial support.

REFERENCES

(1) Salem, L.; Rowland, C. The Electronic Properties of Diradicals. *Angew. Chem., Int. Ed. Engl.* **1972**, *11* (2), 92–111.

(2) Diradicals; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982.

(3) Stuyver, T.; Chen, B.; Zeng, T.; Geerlings, P.; De Proft, F.; Hoffmann, R. Do Diradicals Behave Like Radicals? *Chem. Rev.* 2019, 119 (21), 11291–11351.

(4) Grützmacher, H.; Breher, F. Odd-Electron Bonds and Biradicals in Main Group Element Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41* (21), 4006–4011.

(5) Breher, F. Stretching Bonds in Main Group Element Compounds — Borderlines between Biradicals and Closed-Shell Species. *Coord. Chem. Rev.* **2007**, *251*, 1007–1043.

(6) Abe, M.; Ye, J.; Mishima, M. The Chemistry of Localized Singlet 1,3-Diradicals (Biradicals): From Putative Intermediates to Persistent Species and Unusual Molecules with a π -Single Bonded Character. *Chem. Soc. Rev.* **2012**, *41* (10), 3808–3820.

(7) González-Gallardo, S.; Breher, F. Main Group Biradicaloids. In *Comprehensive Inorganic Chemistry II*; Elsevier: Amsterdam, 2013; Vol. 1, pp 413–455.

(8) Abe, M. Diradicals. Chem. Rev. 2013, 113 (9), 7011-7088.

(9) Gryn'ova, G.; Coote, M. L.; Corminboeuf, C. Theory and Practice of Uncommon Molecular Electronic Configurations. *WIREs Comput. Mol. Sci.* 2015, 5 (6), 440–459.

(10) Schulz, A. Group 15 Biradicals: Synthesis and Reactivity of Cyclobutane-1,3-Diyl and Cyclopentane-1,3-Diyl Analogues. *Dalton Trans.* **2018**, 47 (37), 12827–12837.

(11) Gopalakrishna, T. Y.; Zeng, W.; Lu, X.; Wu, J. From Open-Shell Singlet Diradicaloids to Polyradicaloids. *Chem. Commun.* **2018**, *54* (18), 2186–2199.

(12) Hollett, J. W.; Gill, P. M. W. The Two Faces of Static Correlation. J. Chem. Phys. 2011, 134 (11), 114111.

(13) Cramer, C. J. Essentials of Computational Chemistry: Theories and Models; John Wiley & Sons, Ltd: Chichester, UK, 2004.

(14) Noodleman, L. Valence Bond Description of Antiferromagnetic Coupling in Transition Metal Dimers. J. Chem. Phys. **1981**, 74 (10), 5737–5743.

(15) Michl, J.; Bonačić-Koutecký, V. Biradicals and Biradicaloids: A Unified View. *Tetrahedron* **1988**, 44 (24), 7559–7585.

(16) Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. A P_2C_2 Four-Membered Ring with Unusual Bonding—Synthesis, Structure, and Ring Opening of a 1,3-Diphosphacyclobutane-2,4-Diyl. *Angew. Chem., Int. Ed. Engl.* **1995**, *34* (5), 555–557.

(17) Schoeller, W. W.; Begemann, C.; Niecke, E.; Gudat, D. Electronic Structure of the 2.4-Diphosphacyclobutane-Diyl-1.3 and Substituted Derivatives. *J. Phys. Chem. A* **2001**, *105* (47), 10731–10738.

(18) Zhang, S.-H.; Xi, H.-W.; Lim, K. H.; Meng, Q.; Huang, M.-B.; So, C.-W. Synthesis and Characterization of a Singlet Delocalized 2,4-Diimino-1,3-Disilacyclobutanediyl and a Silylenylsilaimine. *Chem. - Eur. J.* **2012**, *18* (14), 4258–4263.

(19) Demeshko, S.; Godemann, C.; Kuzora, R.; Schulz, A.; Villinger, A. An Arsenic-Nitrogen Biradicaloid: Synthesis, Properties, and Reactivity. *Angew. Chem., Int. Ed.* **2013**, *52* (7), 2105–2108.

(20) Hinz, A.; Schulz, A.; Villinger, A. A Mixed Arsenic-Phosphorus Centered Biradicaloid. *Angew. Chem., Int. Ed.* 2015, 54 (2), 668–672.
(21) Rottschäfer, D.; Neumann, B.; Stammler, H.-G.; Ghadwal, R. S. N -Heterocyclic Vinylidene-Stabilized Phosphorus Biradicaloid. *Chem. Eur. J.* 2017, 23 (38), 9044–9047. (22) Li, Z.; Chen, X.; Andrada, D. M.; Frenking, G.; Benkő, Z.; Li, Y.; Harmer, J. R.; Su, C.-Y.; Grützmacher, H. $(L)_2C_2P_2$: Dicarbondiphosphide Stabilized by N-Heterocyclic Carbenes or Cyclic Diamido Carbenes. *Angew. Chem., Int. Ed.* **2017**, *56* (21), 5744–5749.

(23) Rottschäfer, D.; Neumann, B.; Stammler, H.; Kishi, R.; Nakano, M.; Ghadwal, R. S. A Phosphorus Analogue of p-Quinodimethane with a Planar P_4 Ring: A Metal-Free Diphosphorus Source. *Chem.* - *Eur. J.* **2019**, *25* (13), 3244–3247.

(24) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. Singlet Diradicals: From Transition States to Crystalline Compounds. *Science* **2002**, *295* (5561), 1880–1881.

(25) Sugiyama, H.; Ito, S.; Yoshifuji, M. Synthesis of a 1,3-Diphosphacyclobutane-2,4-Diyl from Mes*CP. *Angew. Chem., Int. Ed.* **2003**, 42 (32), 3802–3804.

(26) Cox, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J. M. A 1,3-Diaza-2,4-Distannacyclobutanediide: Synthesis, Structure, and Bonding. *Angew. Chem., Int. Ed.* **2004**, *43* (34), 4500–4504.

(27) Cui, C.; Brynda, M.; Olmstead, M. M.; Power, P. P. Synthesis and Characterization of the Non-Kekulé, Singlet Biradicaloid $Ar'Ge(\mu$ -NSiMe₃)₂GeAr' (Ar' = 2,6-Dipp₂C₆H₃, Dipp = 2,6-*i*-Pr₂C₆H₃). J. Am. Chem. Soc. **2004**, 126 (21), 6510–6511.

(28) Wang, X.; Peng, Y.; Olmstead, M. M.; Fettinger, J. C.; Power, P. P. An Unsymmetric Oxo/Imido-Bridged Germanium-Centered Singlet Diradicaloid. *J. Am. Chem. Soc.* **2009**, *131* (40), 14164–14165.

(29) Henke, P.; Pankewitz, T.; Klopper, W.; Breher, F.; Schnöckel, H. Snapshots of the Al-Al σ -Bond Formation Starting from {AlR₂} Units: Experimental and Computational Observations. *Angew. Chem., Int. Ed.* **2009**, 48 (43), 8141–8145.

(30) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. Access to a Stable Si_2N_2 Four-Membered Ring with Non-Kekule' Singlet Biradical Character from a Disilyne. *J. Am. Chem. Soc.* **2011**, *133* (32), 12478–12481.

(31) Beweries, T.; Kuzora, R.; Rosenthal, U.; Schulz, A.; Villinger, A. $[P(\mu-NTer)]_2$: A Biradicaloid That Is Stable at High Temperature. *Angew. Chem., Int. Ed.* **2011**, 50 (38), 8974–8978.

(32) Hinz, A.; Kuzora, R.; Rosenthal, U.; Schulz, A.; Villinger, A. Activation of Small Molecules by Phosphorus Biradicaloids. *Chem. - Eur. J.* **2014**, *20* (45), 14659–14673.

(33) Hinz, A.; Schulz, A.; Seidel, W. W.; Villinger, A. A New Class of Azadipnictiridines Generated by an Unusual Rearrangement Reaction. *Inorg. Chem.* **2014**, *53* (21), 11682–11690.

(34) Hinz, A.; Schulz, A.; Villinger, A. Tunable Cyclopentane-1,3-Diyls Generated by Insertion of Isonitriles into Diphosphadiazanediyls. J. Am. Chem. Soc. **2015**, 137 (31), 9953–9962.

(35) Hinz, A.; Schulz, A.; Villinger, A. Stable Heterocyclopentane-1,3-Diyls. Angew. Chem., Int. Ed. 2015, 54 (9), 2776–2779.

(36) Brückner, A.; Hinz, A.; Priebe, J. B.; Schulz, A.; Villinger, A. Cyclic Group 15 Radical Cations. *Angew. Chem., Int. Ed.* **2015**, 54 (25), 7426–7430.

(37) Hinz, A.; Schulz, A.; Villinger, A. Metal-Free Activation of Hydrogen, Carbon Dioxide, and Ammonia by the Open-Shell Singlet Biradicaloid $[P(\mu-NTer)]_2$. Angew. Chem., Int. Ed. **2016**, 55 (40), 12214–12218.

(38) Hinz, A.; Schulz, A.; Villinger, A. On the Behaviour of Biradicaloid $[P(\mu-NTer)]_2$ towards Lewis Acids and Bases. *Chem. Commun.* **2016**, 52 (37), 6328–6331.

(39) Hinz, A.; Kuzora, R.; Rölke, A.-K.; Schulz, A.; Villinger, A.; Wustrack, R. Synthesis of a Silylated Phosphorus Biradicaloid and Its Utilization in the Activation of Small Molecules. *Eur. J. Inorg. Chem.* **2016**, 2016 (22), 3611–3619.

(40) Bresien, J.; Hinz, A.; Schulz, A.; Villinger, A. As-N and As-N-P Cage Compounds Generated by [2 + 2] Addition of Diazenes and Diphosphenes to Diarsadiazanediyls. *Eur. J. Inorg. Chem.* **2018**, 2018 (15), 1679–1682.

(41) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. Chiroptical Molecular Switches. *Chem. Rev.* **2000**, *100* (5), 1789–1816.

(42) Russew, M.-M.; Hecht, S. Photoswitches: From Molecules to Materials. *Adv. Mater.* **2010**, *22* (31), 3348–3360.

pubs.acs.org/joc

(43) Göstl, R.; Senf, A.; Hecht, S. Remote-Controlling Chemical Reactions by Light: Towards Chemistry with High Spatio-Temporal Resolution. *Chem. Soc. Rev.* **2014**, *43* (6), 1982–1996.

(44) Bléger, D.; Hecht, S. Visible-Light-Activated Molecular Switches. Angew. Chem., Int. Ed. 2015, 54 (39), 11338–11349.

(45) Zhang, J. L.; Zhong, J. Q.; Lin, J. D.; Hu, W. P.; Wu, K.; Xu, G. Q.; Wee, A. T. S.; Chen, W. Towards Single Molecule Switches. *Chem. Soc. Rev.* **2015**, *44* (10), 2998–3022.

(46) Bresien, J.; Kröger-Badge, T.; Lochbrunner, S.; Michalik, D.; Müller, H.; Schulz, A.; Zander, E. A Chemical Reaction Controlled by Light-Activated Molecular Switches Based on Hetero-Cyclopentanediyls. *Chem. Sci.* **2019**, *10* (12), 3486–3493.

(47) Krumlacher, W.; Siegl, H.; Hassler, K. Hypersilyl Compounds of Elements of Group 15. In *Organosilicon Chemistry IV: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2000; pp 367–371.

(48) Kira, M.; Iwamoto, T. Silyl Migrations. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons, Ltd: Chichester, UK, 2001; Vol. 3, pp 853–948.

(49) Pyykkö, P.; Atsumi, M. Molecular Double-Bond Covalent Radii for Elements Li-E112. *Chem. - Eur. J.* 2009, 15 (46), 12770–12779.

(50) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865– 3868.

(51) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, 78 (7), 1396– 1396.

(52) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7 (18), 3297–3305.

(53) Hegarty, D.; Robb, M. A. Application of Unitary Group Methods to Configuration Interaction Calculations. *Mol. Phys.* **1979**, 38 (6), 1795–1812.

(54) Eade, R. H. A.; Robb, M. A. Direct Minimization in Mc Scf Theory. the Quasi-Newton Method. *Chem. Phys. Lett.* **1981**, *83* (2), 362–368.

(55) Schlegel, H. B.; Robb, M. A. MC SCF Gradient Optimization of the $H_2CO \rightarrow H_2$ + CO Transition Structure. *Chem. Phys. Lett.* **1982**, 93 (1), 43–46.

(56) Bernardi, F.; Bottoni, A.; McDouall, J. J. W.; Robb, M. A.; Schlegel, H. B. MCSCF Gradient Calculation of Transition Structures in Organic Reactions. *Faraday Symp. Chem. Soc.* **1984**, *19* (4), 137.

(57) Siegbahn, P. E. M. A New Direct CI Method for Large CI Expansions in a Small Orbital Space. *Chem. Phys. Lett.* **1984**, *109* (5), 417–423.

(58) Robb, M. A.; Niazi, U. The Unitary Group Approach to Electronic Structure Computation. In *Reports in Molecular Theory;* Weinstein, H., Náray-Szabó, G., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. 1, pp 23–55.

(59) Frisch, M. J.; Ragazos, I. N.; Robb, M. A.; Schlegel, H. B. An Evaluation of Three Direct MC-SCF Procedures. *Chem. Phys. Lett.* **1992**, *189* (6), 524–528.

(60) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, H. B. A Direct Derivative MC-SCF Procedure. *Chem. Phys. Lett.* **1996**, 250 (3–4), 373–378.

(61) Klene, M.; Robb, M. A.; Frisch, M. J.; Celani, P. Parallel Implementation of the CI-Vector Evaluation in Full CI/CAS-SCF. *J. Chem. Phys.* **2000**, *113* (14), 5653–5665.

(62) Miliordos, E.; Ruedenberg, K.; Xantheas, S. S. Unusual Inorganic Biradicals: A Theoretical Analysis. *Angew. Chem., Int. Ed.* **2013**, 52 (22), 5736–5739.

(63) Bresien, J.; Hinz, A.; Schulz, A.; Villinger, A. Trapping of Transient, Heavy Pnictogen-Centred Biradicals. *Dalton Trans.* 2018, 47 (13), 4433-4436.

(64) Su, Y.-T.; Huang, Y.-H.; Witek, H. A.; Lee, Y.-P. Infrared Absorption Spectrum of the Simplest Criegee Intermediate CH_2OO . *Science* **2013**, *340* (6129), 174–176.

(65) Doehnert, D.; Koutecky, J. Occupation Numbers of Natural Orbitals as a Criterion for Biradical Character. Different Kinds of Biradicals. J. Am. Chem. Soc. **1980**, 102 (6), 1789–1796.

(66) Stuyver, T.; Zeng, T.; Tsuji, Y.; Geerlings, P.; De Proft, F. Diradical Character as a Guiding Principle for the Insightful Design of Molecular Nanowires with an Increasing Conductance with Length. *Nano Lett.* **2018**, *18* (11), 7298–7304.

(67) Glendening, E. D.; Weinhold, F. Natural Resonance Theory: I. General Formalism. J. Comput. Chem. 1998, 19 (6), 593-609.

(68) Riplinger, C.; Neese, F. An Efficient and near Linear Scaling Pair Natural Orbital Based Local Coupled Cluster Method. *J. Chem. Phys.* **2013**, *138* (3), 034106.

(69) Liakos, D. G.; Sparta, M.; Kesharwani, M. K.; Martin, J. M. L.; Neese, F. Exploring the Accuracy Limits of Local Pair Natural Orbital Coupled-Cluster Theory. *J. Chem. Theory Comput.* **2015**, *11* (4), 1525–1539.

(70) Riplinger, C.; Pinski, P.; Becker, U.; Valeev, E. F.; Neese, F. Sparse Maps—A Systematic Infrastructure for Reduced-Scaling Electronic Structure Methods. II. Linear Scaling Domain Based Pair Natural Orbital Coupled Cluster Theory. J. Chem. Phys. 2016, 144 (2), 024109.

(71) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Towards the Online Computer-Aided Design of Catalytic Pockets. *Nat. Chem.* **2019**, *11* (10), 872–879.

(72) London, F. Théorie Quantique Des Courants Interatomiques Dans Les Combinaisons Aromatiques. J. Phys. Radium 1937, 8 (10), 397-409.

(73) McWeeny, R. Perturbation Theory for the Fock-Dirac Density Matrix. *Phys. Rev.* **1962**, *126* (3), 1028–1034.

(74) Ditchfield, R. Self-Consistent Perturbation Theory of Diamagnetism. *Mol. Phys.* **1974**, *27* (4), 789-807.

(75) Wolinski, K.; Hinton, J. F.; Pulay, P. Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations. *J. Am. Chem. Soc.* **1990**, *112* (23), 8251–8260.

(76) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. A Comparison of Models for Calculating Nuclear Magnetic Resonance Shielding Tensors. J. Chem. Phys. **1996**, 104 (14), 5497–5509.

(77) Fischer, C. B.; Xu, S.; Zipse, H. Steric Effects in the Uncatalyzed and DMAP-Catalyzed Acylation of Alcohols—Quantifying the Window of Opportunity in Kinetic Resolution Experiments. *Chem. - Eur. J.* **2006**, *12* (22), 5779–5784.

(78) Reiß, F.; Schulz, A.; Villinger, A.; Weding, N. Synthesis of Sterically Encumbered 2,4-Bis-m-Terphenyl-1,3-Dichloro-2,4-Cyclo-Dipnictadiazanes [m-TerNPnCl]₂, (Pn = P, As). *Dalton Trans.* **2010**, 39 (41), 9962–9972.

(79) Bresien, J.; Hering-Junghans, C.; Schulz, A.; Thomas, M.; Villinger, A. Reactivity of $TerN(SiMe_3)BiCl_2$ —Synthesis of an Aminobismuthenium Cation and $TerN(SiMe_3)Bi(N_3)_2$. Organometallics **2018**, 37 (15), 2571–2580.

(80) Kuzora, R.; Schulz, A.; Villinger, A.; Wustrack, R. Hypersilylated Cyclodiphosphadiazanes and Cyclodiphosphadiazenium Salts. *Dalton Trans.* **2009**, No. 42, 9304–9311.

(81) Feldmeier, C.; Bartling, H.; Riedle, E.; Gschwind, R. M. LED Based NMR Illumination Device for Mechanistic Studies on Photochemical Reactions – Versatile and Simple, yet Surprisingly Powerful. J. Magn. Reson. 2013, 232, 39–44.

(82) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, 71 (1), 3–8.

(83) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71 (1), 3–8.

(84) Sheldrick, G. M. SADABS; University of Göttingen: Germany, 2004.

(85) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Peterson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision E.01; Gaussian Inc.: Wallingford, CT, 2013.

(86) Neese, F. Software Update: The ORCA Program System, Version 4.0. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8 (1), e1327.

(87) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO* 6.0. Theoretical Chemistry Institute; University of Wisconsin: Madison, WI, 2013.

(88) Carpenter, J. E.; Weinhold, F. Analysis of the Geometry of the Hydroxymethyl Radical by the "Different Hybrids for Different Spins" Natural Bond Orbital Procedure. *J. Mol. Struct.: THEOCHEM* **1988**, 169, 41–62.

(89) Weinhold, F.; Carpenter, J. E. The Natural Bond Orbital Lewis Structure Concept for Molecules, Radicals, and Radical Ions. In *The Structure of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Springer: Boston, MA, 1988; pp 227–236.

(90) Weinhold, F.; Landis, C. R. Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective; Cambridge University Press: Cambridge, UK, 2005.

(91) Weinhold, F.; Landis, C. R. Discovering Chemistry with Natural Bond Orbitals; John Wiley & Sons, Inc.: Hoboken, NJ, 2012.

(92) Weinhold, F.; Landis, C. R.; Glendening, E. D. What Is NBO Analysis and How Is It Useful? *Int. Rev. Phys. Chem.* **2016**, *35* (3), 399-440.

(93) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, 132 (15), 154104.

(94) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 2011, 32 (7), 1456–1465.

(95) Jameson, C. J.; De Dios, A.; Keith Jameson, A. Absolute Shielding Scale for ³¹P from Gas-Phase NMR Studies. *Chem. Phys. Lett.* **1990**, *167* (6), 575–582.

(96) van Wüllen, C. A Comparison of Density Functional Methods for the Calculation of Phosphorus-31 NMR Chemical Shifts. *Phys. Chem. Chem. Phys.* **2000**, 2 (10), 2137–2144.

(97) Wu, S.; Huang, J.; Gazzarrini, S.; He, S.; Chen, L.; Li, J.; Xing, L.; Li, C.; Chen, L.; Neochoritis, C. G.; et al. Isocyanides as Influenza A Virus Subtype H5N1 Wild-Type M2 Channel Inhibitors. *ChemMedChem* **2015**, *10* (11), 1837–1845.