

Cycloaddition of Alkenes and Alkynes to the P-centered Singlet Biradical $[P(\mu\text{-N}Ter)]_2$

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Dedicated to Prof. Dr. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The reaction of biradical $[P(\mu\text{-N}Ter)]_2$ (**1**, Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) towards different alkenes (R = 2,3-dimethyl-butadiene, 2,5-dimethyl-2,4-hexadiene, 1,7-octadiene, 1,4-cyclohexadiene) and alkynes (R = 1,4-diphenyl-1,3-butadiyne) was studied experimentally. Although these olefins can react in different ways, only [2+2] cycloaddition products (**1R**) were observed. The reaction with 2,3-dimethylbutadiene also led to the [2+2] product (**1dmb**). Thermal treatment of **1dmb** above 140 °C resulted in the re-

covery of biradical **1** upon homolytic bond cleavage of the two P–C bonds and the release of 2,3-dimethylbutadiene. In contrast to this reaction, all other [2+2] additions products (**1R**, R = 1,7-octadiene, 1,4-cyclohexadiene, 1,4-diphenyl-1,3-butadiyne) began to decompose at temperatures between 200 °C and 300 °C. Only unidentified products were obtained but no temperature-controlled equilibrium reactions were observed. Computations were carried out to shed light into the formal [2+2] as well as the possible [4+2] addition reaction.

Introduction

Biradicals are known as intermediates in bond formation and bond cleavage processes.^[1–4] Therefore in the past three decades, detailed investigations of their chemistry have attracted increasing interest,^[5–28] especially the synthesis, characterization and reactivity of singlet biradicals derived from cyclobutanediyls by isolobal replacement of carbon atoms by other main group elements.^[2,4,5,29] In 1995 *Niecke* et al. synthesized and isolated the first singlet biradical, a C_2P_2 four-membered carbon centred biradical.^[30] The *Niecke* group has extensively studied the reactivity of this biradical with respect to ring-opening reactions, isomerization, redox activity and reactions with small molecules.^[31–35] In 2002 *Bertrand* et al. synthesized a P_2B_2 cyclobutanediyl and investigated the reactivity towards small molecules and hydrazides.^[17,36,37] From a phosphalkyne as starting material, *Yoshifuji* et al. could prepare a novel 1,3-diphosphacyclobutane-2,4-diyl, which is astonishingly stable towards polar molecules such as water or alcohols.^[38] The first biradical containing heavier group 14 elements was described by the groups of *Power* and *Lappert* who synthesized a 1,3-diaza-2,4-digermacyclobutane-2,4-diyl

$[RGe(\mu\text{-NSiMe}_3)]_2$ ^[39] (R = 2,6-Dipp₂C₆H₃, Dipp = 2,6-*i*Pr₂C₆H₃) and a 1,3-diaza-2,4-distannacyclobutane-2,4-diyl $[ClSn(\mu\text{-NSiMe}_3)]_2$, respectively.^[40] 2009 *Schnöckel* et al. extended the group of singlet biradicals by introducing the heteroatom Al.^[41] Two years later *Sekiguchi* et al. reported a silicon-based biradical $[Dsi_2iPrSi(\mu\text{-N}Ar)]_2$ [$Dsi = CH(SiMe_3)_2$]^[42] and again one year later the group of *So* reported an amidinate-stabilized silicon-based Si_2C_2 biradical.^[43] The groups of *Grützmacher*^[44] and *Ghadwal*^[45] succeeded in preparing one of the first phosphorus-based 1,3-diphosphacyclobutane-1,3-diyls.

Open-shell singlet biradicals of the type $[E(\mu\text{-NR})]_2$ (E = pnictogen, R = Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl, Hypersilyl = bis-tris(trimethylsilyl)silyl) containing only group 15 elements were introduced by our group.^[46–49] $[P(\mu\text{-N}Ter)]_2$ is a thermally very robust biradical which can be generated in very good yields by reducing $[CIP(\mu\text{-N}Ter)]_2$ with magnesium turnings. With $[P(\mu\text{-N}Ter)]_2$ in hands, we studied its reactivity towards molecules bearing single, double and triple bonds.^[46,47,56–65,48,66–71,49–55] We also succeeded in preparing and isolate the arsenic homologue $[As(\mu\text{-N}Ter)]_2$ ^[47] as well as the mixed arsenic–phosphorus-centred biradical $[P(\mu\text{-N}Ter)_2As]$.^[72] The reactivity of the biradical $[E(\mu\text{-N}Ter)]_2$ (E = P, As) towards small molecules like acetone, acetonitrile, CO, CO₂, H₂, alkenes and alkynes has been investigated extensively.^[48] As depicted in Scheme 1, alkenes and alkynes add easily to the $[P(\mu\text{-N}Ter)]_2$ biradical in a [2+2] cycloaddition reaction (**C** and **E**). However, alkynes often display an unusual rearrangement to an azaphosphiridine isomer (**D**) depending on the size of the substituent.^[58]

Herein we report on reactions of small organic hydrocarbons containing multiple double or triple bonds since we were interested in exploring the possibility of [2+2] and/or [4+2] cycloaddition with the biradical $[P(\mu\text{-N}Ter)]_2$ to form new heterocycles. For example, it is known that 2,3-dimethylbutadiene can

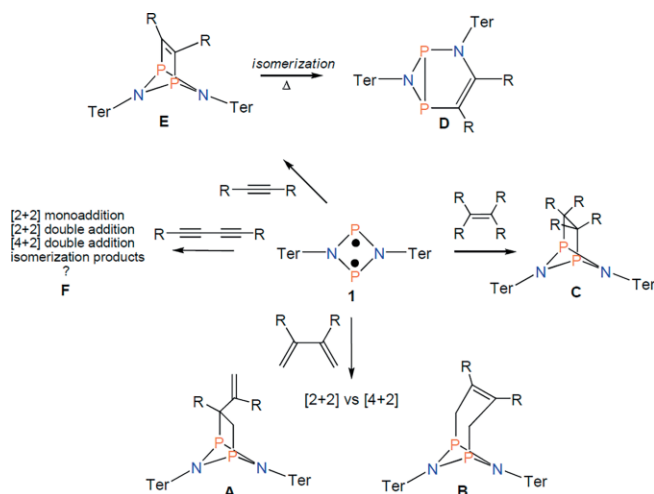
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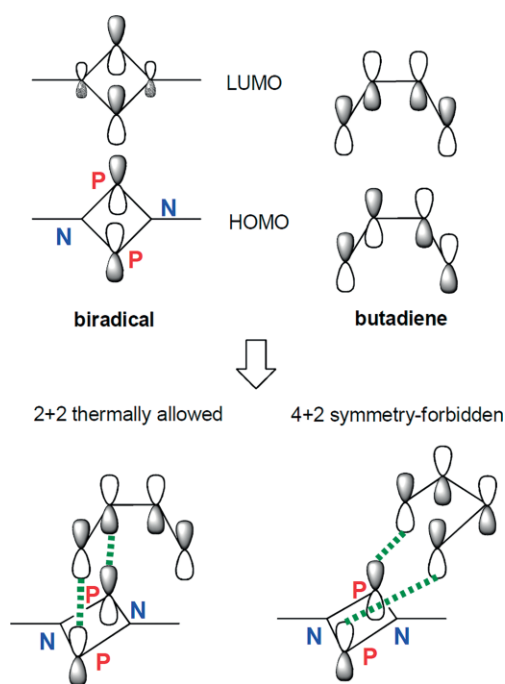
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201900191> or from the author.

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Scheme 1. The reaction of **1** with different small molecules containing alkenes and alkynes.

react either in a [4+2] Diels–Alder reaction, e.g. with trans-stilbene, forming a six-membered ring or in a [2+2] addition reaction with e.g. ketenes, forming four-membered heterocycles.^[73–76] Furthermore, it was of interest to study double cycloaddition reactions with two $[P(\mu\text{-N}Ter)]_2$ molecules when non-conjugated dienes were utilized. Additionally, in the case of diynes, it was necessary to study also the above-mentioned insertion reaction that might follow the [2+2] addition as shown in Scheme 1 (**E** \rightarrow **D**). As depicted in Scheme 2, a [4+2] cycloaddition reaction should be symmetry forbidden, while a [2+2] cycloaddition is thermally allowed according to simple MO considerations.



Scheme 2. Qualitative MO Scheme of the [2+2] and [4+2] cycloaddition.

Results and Discussion

Synthesis and Characterization

All reactions of $[P(\mu\text{-N}Ter)]_2$ (**1**) with dienes (2,3-dimethylbutadiene = **dmb**, 2,5-dimethyl-2,4-hexadiene = **dh**, 1,7-octadiene = **od**, 1,4-cyclohexadiene = **ch4**) and diynes (1,4-diphenyl-1,3-butadiyne = **db**) were carried out in benzene at room temperature (see Supporting Information). In the first series of experiments, both conjugated dienes (**dmb** and **dh**) were treated with biradical **1**. No addition was observed after 24h in the reaction with the **dh**, presumably due to steric shielding. In contrast, a fast conversion was found for the reaction of **1** with **dmb**. Within hours a new addition product was generated as manifested by ^{31}P solution NMR experiments. However, it takes a rather large excess of **dmb** for a reasonable reaction time. Full conversion of a 1:1 mixture was only obtained after two weeks. The new addition product was characterized by two doublets (233.6 and 230.2 ppm) with a coupling constant of 7 Hz (Table 1) in the ^{31}P solution NMR spectrum (298.1 K C_6D_6) that can be attributed to an asymmetric addition of **dmb**, indicating the formation of the [2+2] product (Scheme 1, species **A**). The [4+2] addition can be ruled out since no symmetric product with one ^{31}P resonance was detected. The NMR shifts are all within the expected range of such addition compounds (cf. **1et** ppm 223, Figure 2).^[55] Work-up of the raw product **1dmb** afforded a yellow solid in almost quantitative yield, which could be characterized as the [2+2]-cycloaddition product **1dmb**.

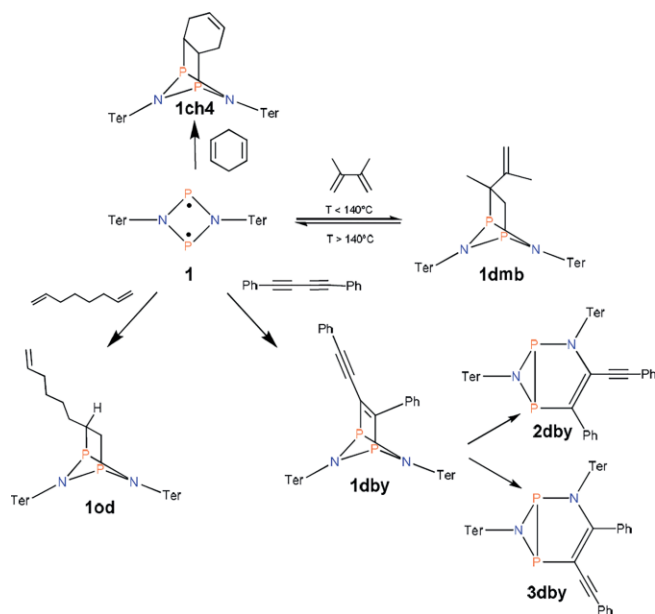
1dmb exhibits interesting thermal properties. Unlike all hitherto known alkene and alkyne addition products, **dmb** can be removed from the phosphorus biradical by heating up pure solid **1dmb** to 140 °C (Scheme 3). The progress of this reaction can be followed easily by the eyes, as solid **1dmb** changes its color from pale yellow to intense orange. The retrieval of pure biradical **1** was verified by ^{31}P NMR spectroscopy ($\delta[^{31}\text{P}] = 276$ ppm, singlet in C_6D_6). Gas-phase IR spectroscopy was used to identify **dmb** as the only product in the gas phase and indeed no other decomposition products could be detected (see Figure S1, Supporting Information). For this IR experiment, **1dmb** was heated to 140 °C in a static vacuum for 15 minutes and then flooded with argon and the gas phase transferred into a gas IR cell.

In the next series of experiments, we treated long-chain, non-conjugated aliphatic dienes such as 1,7-octadiene (**1od**). Again, we started with stoichiometric amounts in a 1:1 as well as a 2:1 ratio (biradical **1:1od**). Although a double substitution with two biradicals appears to be possible for longer dialkenes such as **od**, only the mono addition product **1od** could be observed in ^{31}P NMR experiments (Scheme 3). Obviously, an eight-membered carbon chain is not long enough to allow linking of two sterically demanding biradicals such as **1**. **1od** was isolated as a colorless solid in almost quantitative yield (>99%). Compound **1od** showed a very poor solubility in solvents such as toluene, benzene, dichloromethane and *n*-hexane, which did not allow growing crystals suitable for X-ray structure elucidation. Nevertheless, the solubility was sufficient to

Table 1. ^{13}C and ^{31}P NMR shifts (in ppm) of additions products **1R** for the pure dienes/diynes and the biradical ($\delta[^{31}\text{P}] = 276$ ppm), respectively.

	$\delta^{13}\text{C}$ R	$\delta^{13}\text{C}$ 1R	$\Delta\delta^{13}\text{C}$ 1R/R	$\delta^{31}\text{P}$ 1R	$\Delta\delta^{31}\text{P}$ 1R/R
1dmb	143.6/113.0	55.3/37.6	88.3/75.4	233.6/230.2	42.4/45.8
1ch4	124.5	38.9	85.6	235.2	40.8
1od	138.9/114.4	39.3/33.2	99.6/81.2	229.3 /224	46.7/52
1dby	81.7/74.1	– ^{a)}	–	241.5/227.8	34.5/48.2

a) Could not be assigned.



Scheme 3. Reactions of **1** with dienes and diynes yielding heteroatom substituted [2.1.1]bicyclohexanes in the first reactions step. Alkyne addition product **1dby** isomerizes in a second step upon thermal treatment yielding diphosphaaziridines (**2dby** and **3dby**).

study the compound by NMR techniques. Upon [2+2] addition of od, two isomers were found (see Figure 3).

As shown by computations, there are different types of isomers (Figure 3) with barriers large enough to allow the observation of the NMR signals of two distinct isomers in the ^{31}P (doublets, **isomer 1** $^{31}\text{P}[\delta] = 223.9$ and 229.1 , **isomer 2**: 224.0 and 229.3 ppm) and ^1H spectra ($^1\text{H}[\delta]$: two sets of six singlets signals for twelve different methyl groups, six different per species). Both isomers (1 and 2, Figure 3) were found in the ratio 45:55. Similar to the resonances for 2,3-dimethylbutadiene, the ^{31}P NMR signals (two doublets per isomer) appear at higher field compared to the signal of biradical **1** ($\delta = 276$ ppm). Thermal treatment of **1od** (a probable mixture of isomer 1 and 2) up to 300°C led only to unidentified decomposition products. No reversible od release was observed and therefore biradical **1** could not be recovered (Figure 1, Figure 2, and Figure 3).

1,4-Cyclohexadiene (**ch4**) is known as a trapping agent for radical reactions since it forms benzene upon H_2 release.^[77,78] So it was interesting to see if **ch4** either forms a [2+2] product (**1ch4**) or if H_2 is added to biradical **1** along with the formation of benzene. The latter reaction could be classified as dehydrogenation of **ch4** triggered by the biradical. Experimentally, **ch4**

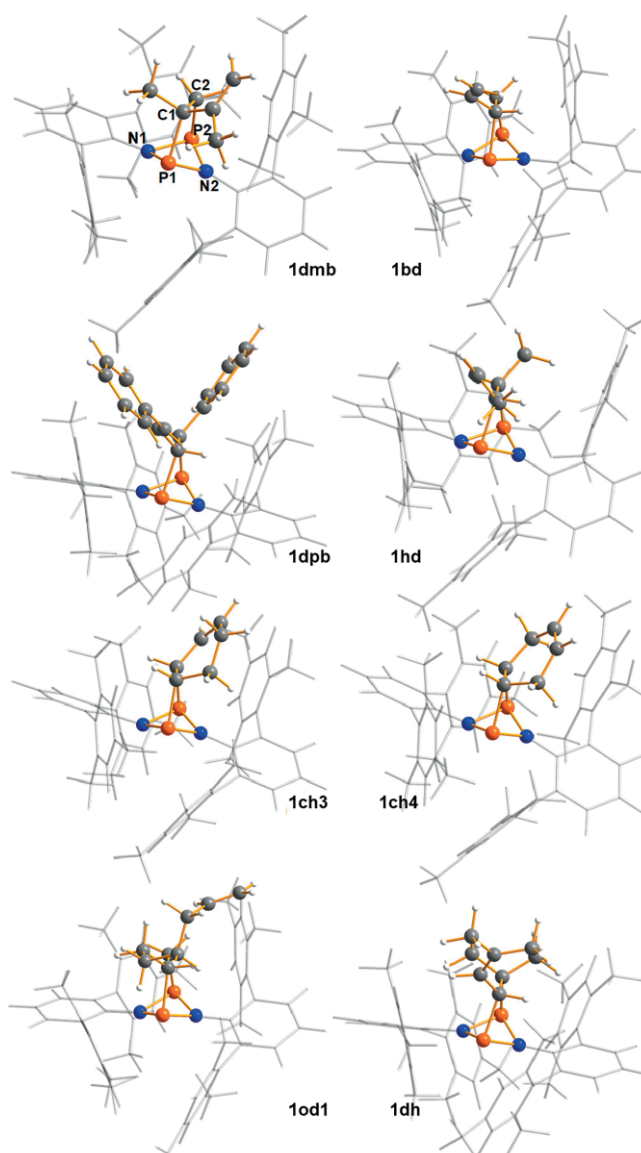


Figure 1. Calculated minimum structures of **1R** (R = dmb = 2,3-dimethylbutadiene, bd = 1,3-butadiene, dpb = diphenyl-1,3-butadiene, hd = 2,4-hexadiene, ch3 = 1,3-cyclohexadiene, ch4 = 1,4-cyclohexadiene, od1 = 1,7-octadiene, dh = 2,5-dimethyl-2,4-hexadiene).

was dropped to a solution of **1** in benzene. The color of the reaction mixture changed immediately from orange to yellow indicating a fast conversion. Again, only the [2+2] cycloaddition product **1ch4** (Scheme 2, Figure 4) could be observed in the ^{31}P NMR spectrum. As expected, the ^{31}P NMR spectrum

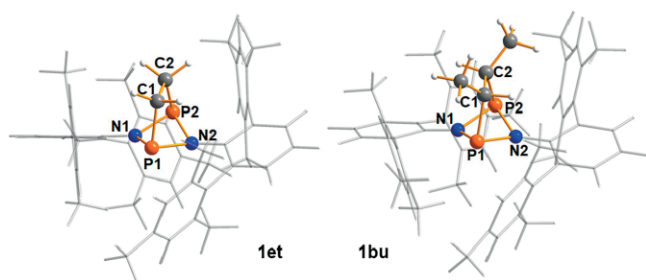


Figure 2. Calculated minimum structures of **1R** (R = et = ethene, bu = 2-butene).

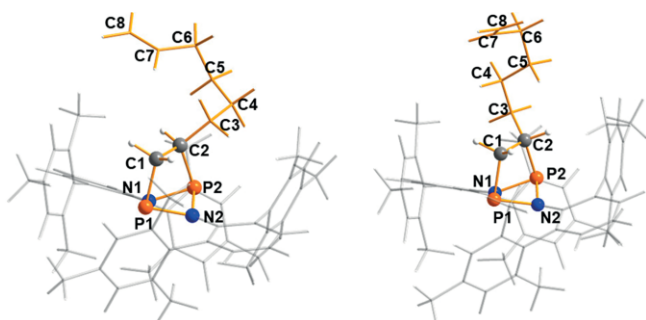


Figure 3. Calculated minimum structures of **1od1** ($\Delta_{\text{rel}}G_{298} = 0$ kcal·mol⁻¹) and **1od2** ($\Delta_{\text{rel}}G_{298} = -6.27$ kcal·mol⁻¹).

displays a singlet resonance at $\delta = 235.1$ ppm, which was assigned to the two chemically equivalent phosphorus atoms. **1ch4** was isolated as colorless solid in good yields (61%). Crystals suitable for X-ray structure analysis were obtained from 1,4-cyclohexadiene as solvent (Figure 4).

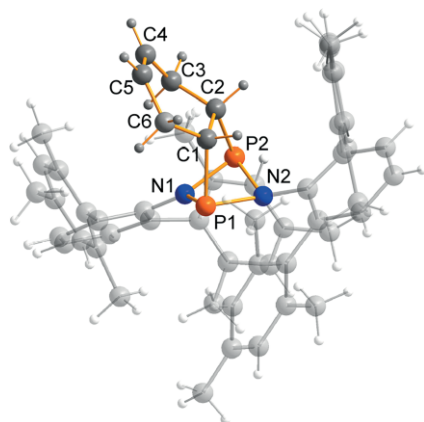


Figure 4. Ball-and-stick representation of the molecular structure of **1ch4** in the crystal. Terphenyl groups are transparent for clarity. Selected bond lengths (Å): P1–N1 1.727(3), P1–N2 1.788(3), P2–N1 1.738(3), P2–N2 1.762(3), P1⋯P2 2.528(2), P1–C1 1.890(4), C1–C2 1.530(5), C4–C5 1.330(7); selected angles (°): P1–N2–P2 90.82(13), N1–P1–N2 80.36(14), N2–P1–C1 89.02(15), N1–P1–N2–P2 27.81(13).

In accord with the computed structure, the molecular structure of **1ch4** in the crystal (space group $P\bar{1}$, $Z = 2$) shows two strongly bent terphenyl substituents forming a pocket large enough to host the [2.1.1]cage compound with a puckered four-membered P_2N_2 -heterocycle [torsion angle (P1–N1–P2–

N2) = 28.3°]. The P1–P2 distance is with 2.528(3) Å significantly elongated compared to the sum of the covalent radii [$\Sigma r_{\text{cov}}(\text{P–P}) = 2.22$ Å]^[79] but significantly shorter than the sum of the van der Waals radii [$\Sigma r_{\text{vdW}}(\text{P}⋯\text{P}) = 3.60$ Å].^[80] All four P–N bond lengths are in the range of a polarized bond [1.727(3)–1.788(3) Å]. Upon addition of **ch4** one of the two double bonds is elongated ranging now in the area of a typical C–C single bond [1.530(5), cf. $\Sigma r_{\text{cov}}(\text{C–C}) = 1.50$ Å], whereas between C4 and C5 the C–C double bond is retained [1.330(7), cf. $\Sigma r_{\text{cov}}(\text{C=C}) = 1.34$ Å].

Analogous to the dienes, 1,4-diphenyl-1,3-butadiyne (**1dby**) was reacted with **1** in benzene and again a fast discoloration was observed. As already discussed for the dienes, also only the [2+2] cycloaddition product (**1dby**) was detected and isolated. There was no evidence for a [4+2] cycloaddition product. **1dby** could be isolated as a slightly orange solid and was fully characterized (yield >99%).

Crystals suitable for X-ray structure analysis could not be obtained. From previous studies, it is known that alkyne products such as **1acetylene** can slowly isomerize to a diphosphaziridine.^[48] Indeed, **1dby** also isomerizes to the two isomeric species **2dby** and **3dby** over 4 weeks as shown in Scheme 2.^[58] Since only one triple bond is involved in the addition reaction, an asymmetric product is formed and therefore the isomerization reaction led to the formation of two different isomers (Scheme 2) as evidenced by ³¹P NMR studies. Two doublet pairs (–61.8 / –84.7 ppm and –58.6 / –90.5 ppm, cf. **1acetylene**: –60.4 / –87.0 ppm) with an integral ratio of 97:3 were detected. According to quantum chemical calculations, two isomers (**2dby** and **3dby**) were found, Figure 6) whereby isomer **2dby** is favored by 3.04 kcal/mol. Both isomerization processes are slightly endergonic with 1.21 and 4.26

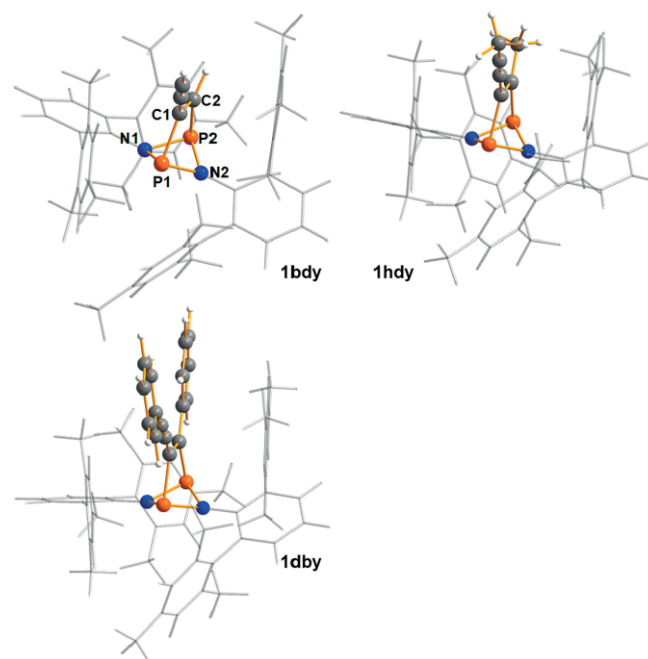


Figure 5. Calculated minimum structures of **1R** (R = bdy = 1,3-butadiyne, hdy = 2,4-hexadiyne, dby = 1,4-diphenyl-1,3-butadiyne).

$\text{kcal}\cdot\text{mol}^{-1}$, respectively (Table 9). **1dby** also showed only unidentified decomposition products when heated above $205\text{ }^\circ\text{C}$. Neither biradical **1** nor free **dbby** was detected (Figure 5 and Figure 6).

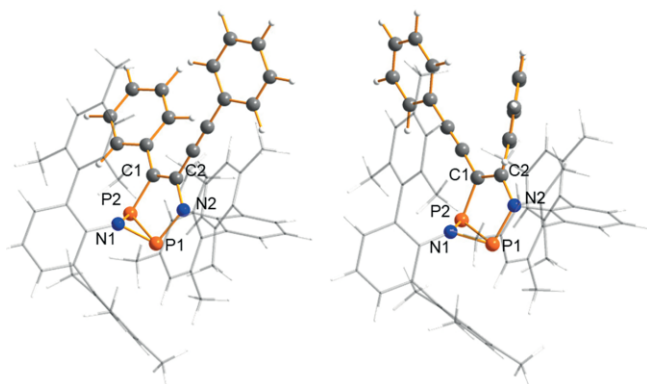


Figure 6. Computed minimum structures of **2dbby** ($\Delta_{\text{rel}}G_{298} = 0\text{ kcal}\cdot\text{mol}^{-1}$) and **3dbby** ($\Delta_{\text{rel}}G_{298} = 3.04\text{ kcal}\cdot\text{mol}^{-1}$).

Computations

To shed light into the structure, thermodynamics and formation of **1R** cage compounds, DFT computations at the

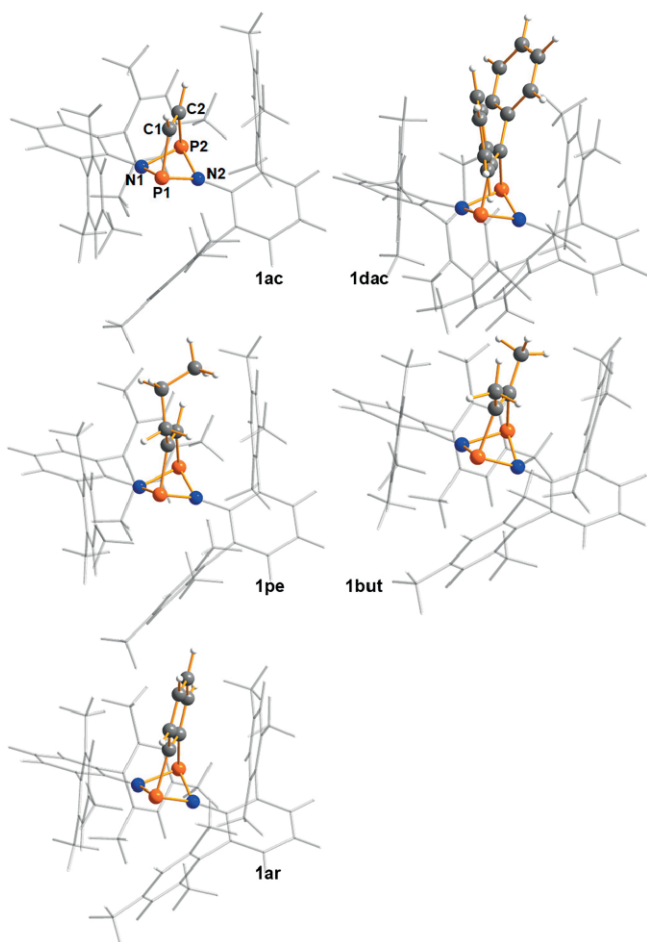


Figure 7. Calculated minimum structures of **1R** (R = ac = acetylene, dac = diphenyl-acetylene, pe = 1-pentyne, but = 2-butyne, ar = aryne).

pbe1pbe/def2svp level of theory including dispersion correction were carried out. In addition to the [2+2] addition products (Figure 1, Figure 2, Figure 5, and Figure 7), we also computed the [4+2] addition products **4R** (Figure 8). The minimum structures of all considered **1R**, as well as **4R** species, are depicted in Figure 1, Figure 2, Figure 5, Figure 7, and Figure 8) along with selected structural data (Table 2, Table 3, Table 4, Table 5, and Table 6). The computed vibrational data of the C–C stretching modes are listed in Table 7.

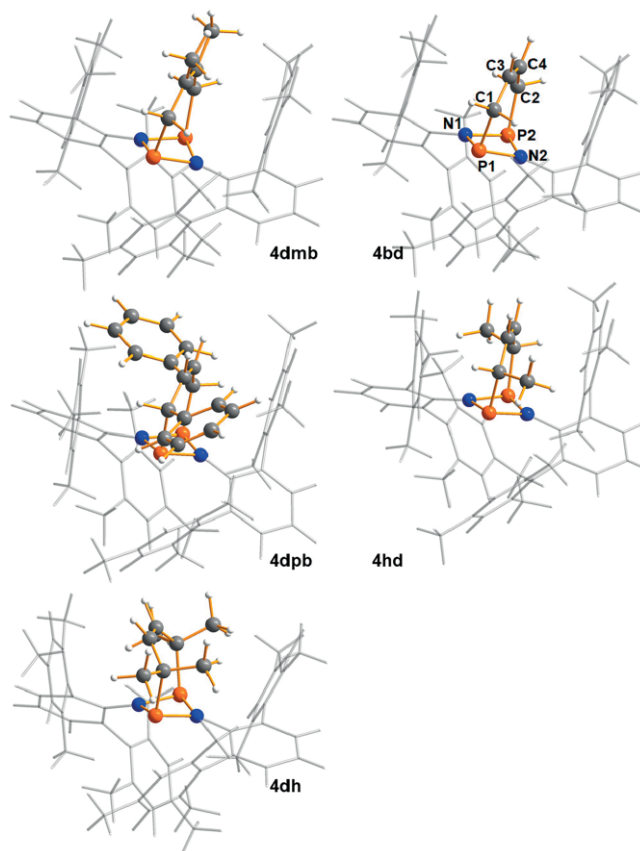


Figure 8. Calculated minimum structures of [4+2] products **4R** (R: dmb = 2,3-dimethylbutadiene, bd = 1,3-butadiene, dhp = 1,4-diphenyl-1,3-butadiene, hd = 2,4-hexadiene, dh = 2,5-dimethyl-2,4-hexadiene).

The most prominent structural feature is the [2.1.1.]bicycle, which is formed upon addition of the alkene/alkyne **R** to the biradical **1**. As expected, in contrast to the biradical **1**, all **1R** and **4R** species display puckered P_2N_2 rings with C–C single bond bridges in case of **1alkene** [$d(\text{C}–\text{C})$ between $1.521–1.548\text{ \AA}$, cf. $\Sigma r_{\text{cov}}(\text{C}–\text{C}) = 1.50\text{ \AA}$] and double bonds for **1alkyne** [$d(\text{C}=\text{C})$ between $1.334–1.403\text{ \AA}$, $\Sigma r_{\text{cov}}(\text{C}=\text{C}) = 1.34\text{ \AA}$].^[79] The [4+2] addition leads to the formation of a [4.1.1.]bicycle featuring now a six-membered heterocycle (C_4P_2). This type of bridging of both phosphorus atoms makes the NPNP four-membered ring less deformed as manifested by dihedral angles ranging only between 6 and 13° . In the absence of experimentally observed structural data, the C–C stretching modes are good indicators for the [2+2] and [4+2] addition reaction, respectively. Upon addition of the alkene/alkyne, the C–C mode is strongly shifted to lower wavenumber ($\Delta\nu_{\text{C}–\text{C}}$ between

Table 2. Selected calculated distances /Å and angles /° for products **1R** (dienes, Figure 1) at the pbe1pbe/def2svp level of theory including dispersion correction.

	P1-N1	P1-N2	P1-C1	P2-C2	C1-C2	Angle 1 ^{a)}	Angle 2 ^{a)}	NPNP
1dmb	1.775	1.753	1.948	1.874	1.537	91.4	93.5	27.7
1bd	1.765	1.769	1.937	1.890	1.526	94.5	94.5	28.4
1dpb	1.760	1.788	1.933	1.933	1.521	95.9	95.2	28.3
1hd	1.778	1.757	1.936	1.903	1.525	95.1	96.8	28.9
1ch3	1.783	1.769	1.898	1.918	1.532	93.0	95.1	28.0
1ch4	1.787	1.760	1.902	1.899	1.537	93.1	95.9	28.0
1od1	1.772	1.769	1.915	1.886	1.526	94.1	94.6	28.5
1dh	1.759	1.801	1.912	1.921	1.548	96.2	94.4	28.2

a) Angle 1 = N1–P1–C1; Angle 2 = N2–P2–C2.

Table 3. Selected calculated distances /Å and angles /° for products **1R** (linear mono alkenes, Figure 2) at the pbe1pbe/def2svp level of theory including dispersion correction.

	P1-N1	P1-N2	P1-C1	P2-C2	C1-C2	Angle 1 ^{a)}	Angle 2 ^{a)}	NPNP
1et	1.750	1.803	1.892	1.895	1.527	94.3	92.5	27.5
1bu	1.763	1.797	1.906	1.907	1.528	95.9	94.8	28.5

a) Angle 1 = N1–P1–C1; Angle 2 = N2–P2–C2.

Table 4. Selected calculated distances /Å and angles /° for products **1R** (linear diynes, Figure 5) at the pbe1pbe/def2svp level of theory including dispersion correction.

	P1-N1	P1-N2	P1-C1	P2-C2	C1-C2	Angle α ^{a)}	Angle β ^{a)}	NPNP
1bdy	1.776	1.764	1.942	1.896	1.344	90.7	92.2	29.9
1hdy	1.764	1.787	1.923	1.906	1.351	92.4	92.5	30.4
1dby	1.763	1.774	1.927	1.914	1.360	91.9	92.8	30.0

a) Angle α = N1–P1–C1; Angle β = N2–P2–C2.**Table 5.** Selected calculated distances /Å and angles /° for products **1R** (mono alkynes, Figure 7) at the pbe1pbe/def2svp level of theory including dispersion correction.

	P1-N1	P1-N2	P1-C1	P2-C2	C1-C2	Angle 1 ^{a)}	Angle 2 ^{a)}	NPNP
1ac	1.790	1.762	1.905	1.904	1.334	90.2	92.4	30.7
1dac	1.758	1.784	1.921	1.925	1.351	92.9	91.8	30.4
1pe	1.787	1.760	1.924	1.890	1.339	91.1	92.7	31.1
1but	1.771	1.785	1.907	1.907	1.343	92.9	92.9	31.5
1ar	1.772	1.787	1.883	1.883	1.403	91.8	91.8	29.3

a) Angle 1 = N1–P1–C1; Angle 2 = N2–P2–C2.

Table 6. Calculated distances /Å and angles /° for [4+2] products **4R** (Figure 8) at the pbe1pbe/def2svp level of theory including dispersion correction.

	P1-N1	P1-N2	P1-C1	P2-C2	C3-C4	Angle 1 ^{a)}	Angle 2 ^{a)}	NPNP
1dmb	1.741	1.783	1.841	1.847	1.352	108.2	107.5	10.7
1bd	1.745	1.784	1.847	1.852	1.340	107.4	107.0	7.7
1dpb	1.761	1.771	1.886	1.874	1.338	103.1	104.4	6.7
1hd	1.759	1.774	1.860	1.860	1.338	106.6	106.6	7.4
1dh	1.750	1.787	1.925	1.919	1.335	107.6	112.1	12.9

a) Angle 1 = N1–P1–C1; Angle 2 = N2–P2–C2.

400–723 cm⁻¹) in accord with the elongated C–C bond bridging the P₂N₂ heterocycle (Table 7). Upon addition of alkenes as well as alkynes, the C–C bond order is always formally decreased by one, which has a strong influence on the structures of the cage structures.

The structures of the [2 + 2] products of both alkynes and alkenes are very similar. Due to the double bond in the products of the alkyne addition, however, the NPNP ring is slightly more deformed (maximal deviation from planarity as indicated by NPNP dihedral angle 4°, Table 2, Table 3, Table 4, and

Table 7. Calculated C–C distances and vibrational modes of the bridging carbon atoms (C–C stretching mode) in **R** and **1R** product.

R	$\nu_{\text{C-C,R}}$	$\nu_{\text{C-C,1R}}^{\text{a)}$	$\Delta\nu$	$d(\text{C-C})_{\text{R}}$	$d(\text{C-C})_{\text{1R}}$	$\Delta d(\text{C-C})$
Ethene	1717	1005	712	1.331	1.527	0.196
2-butene	1774	1158	616	1.339	1.528	0.189
2,3-Dimethylbutadiene	1694	1168	526	1.345	1.537	0.192
1,3-Butadiene	1682	1091	591	1.340	1.526	0.186
Diphenyl-1,3-butadiene	1708	1069	639	1.353	1.521	0.168
2,4-Hexadiene	1730	1165	565	1.344	1.525	0.181
1,3-Cyclohexadiene	1714	1133	581	1.344	1.532	0.188
1,4-Cyclohexadiene	1746	1155	591	1.336	1.537	0.201
1,7-Octadiene	1745	1022	723	1.334	1.526	0.192
2,5-Dimethyl-2,4-hexadiene	1718	1234	484	1.352	1.548	0.196
Acetylene	2085	1600	485	1.209	1.334	0.126
Diphenylacetylene	2347	1672	675	1.219	1.351	0.133
1-Pentyne	2249	1663	586	1.211	1.339	0.127
2-Butyne	2395	1704	691	1.212	1.343	0.131
1,3-Butadiyne	2131	1627	504	1.216	1.344	0.128
2,4-Hexadiyne	2296	1671	626	1.219	1.351	0.132
Diphenyl-1,3-butadiyne	2268	1639	629	1.220	1.360	0.140
Aryne	2054	1654	400	1.252	1.403	0.151
4+2 Cycloaddition products						
2,3-Dimethylbutadiene	1418	1760	−341	1.480	1.352	−0.128
1,3-Butadiene	1450	1767	−317	1.454	1.340	−0.115
Diphenyl-1,3-butadiene	1410	1776	−366	1.439	1.338	−0.101
2,4-Hexadiene	1341	1778	−437	1.451	1.338	−0.113
2,5-Dimethyl-2,4-hexadiene	1203	1768	−565	1.449	1.335	−0.114
Not in bridging involved double/triple bond ^{b)} in R and 1R						
2,3-Dimethylbutadiene	1694	1733	−39			
1,3-Butadiene	1682	1726	−43			
Diphenyl-1,3-butadiene	1708	1735	−27			
2,4-Hexadiene	1730	1749	−19			
1,3-Cyclohexadiene	1714	1745	−31			
1,4-Cyclohexadiene	1746	1763	−18			
1,7-Octadiene	1745	1739	6			
2,5-Dimethyl-2,4-hexadiene	1718	1758	−40			
1,3-Butadiyne	2131	2207	−76			
2,4-Hexadiyne	2296	2341	−45			
Diphenyl-1,3-butadiyne	2268	2293	−25			

a) This stretching mode is always coupled with vibrations of the cage. b) Second C–C vibrational mode which is almost unaffected upon addition.

Table 5) than in the alkene products. All bond lengths are nearly identical except, of course, between the two bridging carbons.

To get insight into the thermodynamics of the formation process ([2+2] vs. [4+2] product formation), the Gibbs energies of the associated reaction were calculated. In agreement with experiment, all computed [2+2] products are formed in an exergonic process ranging between -7.95 and -20.07 for the **1alkenes** and -31.76 to -92.34 ($\text{kcal}\cdot\text{mol}^{-1}$) for the **1alkynes** (Table 8, Table 9). Obviously, the addition of double bonds is less exergonic than alkyne addition (cf. -14.79 $\text{kcal}\cdot\text{mol}^{-1}$ 2-butene, -29.23 $\text{kcal}\cdot\text{mol}^{-1}$ 2-butyne, cf. Table 8 and Table 9) and ethene addition is energetically favored over the addition of alkenes bearing conjugated and non-conjugated double bonds (cf. -29.43 $\text{kcal}\cdot\text{mol}^{-1}$ ethene, -10.94 $\text{kcal}\cdot\text{mol}^{-1}$ 2,4-hexadiene, Table 8).

With respect to the reversibility of the addition reaction, only the back reaction towards 2,3-dimethylbutadiene with a Gibbs energy of -12.39 $\text{kcal}\cdot\text{mol}^{-1}$ for the [2+2] reaction was

experimentally observed. Interestingly, the [4+2] product (**4R**) formation in case of conjugated alkenes and alkynes is energetically favored in most cases over the [2+2] product (**1R**) for example, **1dmb** -12.39 $\text{kcal}\cdot\text{mol}^{-1}$; **4dmb** -23.73 $\text{kcal}\cdot\text{mol}^{-1}$

Table 8. Calculated Gibbs energies $\Delta_{\text{R}}G_{298}^{\ominus}$ ($\text{kcal}\cdot\text{mol}^{-1}$) for the formation of the [2+2] **1R** and [4+2] product **4R**: **1** + **R** \rightarrow **1R** or **4R** at the pbe1pbe/def2svp level of theory including dispersion correction (order: from least to most exergonic [2+2] products).

R	$\Delta_{\text{R}}G_{298}^{\ominus}(\mathbf{1R})$	$\Delta_{\text{R}}G_{298}^{\ominus}(\mathbf{4R})$
2,5-Dimethyl-2,4-hexadiene ^{a)}	−7.95	10.83
2,4-Hexadiene	−10.94	−11.52
2,3-Ddimethylbutadiene ^{a)}	−12.39	−23.73
Diphenyl-1,3-butadiene	−12.68	−8.03
2-Butene	−14.79	
1,4-Cyclohexadiene ^{a)}	−17.01	
1,7-Octadiene ^{a)}	−21.51	
1,3-Butadiene	−20.23	−25.78
1,3-Cyclohexadiene	−25.00	
Ethene	−29.43	

a) Experimentally tested.

Table 9. Calculated Gibbs energies $\Delta_{\text{R}}G_{298}^{\circ}$ (kcal·mol⁻¹) for isomerization of the **1R** yielding either **2R** or **3R**: **1R** → **2R** or **3R** (Scheme 2) at the pbe1pbe/def2svp level of theory including dispersion correction (order: from least to most exergonic [2+2] products).

R	$\Delta_{\text{R}}G_{298}^{\circ}(\mathbf{1R})$	$\Delta_{\text{R}}G_{298}^{\circ}(\mathbf{2R})$	$\Delta_{\text{R}}G_{298}^{\circ}(\mathbf{3R})$
2-Butyne	-31.76	-3.92 ^{b)}	
2,4-Hexadiyne	-32.60	-1.41	-4.25
1-Pentyne	-32.74	-8.38	-5.36
Diphenylacetylene	-35.91	3.51	^{b)}
Acetylene	-37.70	-10.26	^{b)}
1,3-Butadiyne	-38.17	-1.39	-6.54
Diphenyl-1,3-butadiyne ^{a)}	-40.23	1.21	4.26
Aryne	-92.34	-0.20	^{b)}

a) Experimentally tested. b) Symmetric alkyne hence only one isomer was observed.

(Table 8). Therefore, it can be assumed that the [2+2] addition is kinetically favored over the [4+2] process. As discussed before, the [2+2] alkyne addition products **1alkyne** slowly isomerize to give diphospaaziridines (Scheme 2, isomers **2R** and **3R**).

Although the calculated Gibbs energies for the isomerization process are usually exergonic in case of the alkynes (see Figure 1 reaction **E** → **D**), alkynes having a phenyl group as a substituent are different, since the Gibbs energy for the isomerization to the six-membered heterocycle is slightly endergonic or the gas phase (Table 8 and Table 9). Nevertheless, as already mentioned, an insertion experiment for the reaction with diphenyl-1,3-butadiyne could be observed experimentally.

Conclusions

The cycloaddition reactions of differently substituted dienes and diynes with the open-shell singlet biradical [P(μ-Nter)]₂ was investigated. Experimentally, in all cases only thermally-allowed [2+2] cycloaddition reactions were observed, although thermodynamically the formation of the [4+2] product is mostly energetically favored but symmetry-forbidden. Especially, ³¹P and ¹³C{¹H} NMR spectroscopy is a powerful tool to monitor the cycloaddition reaction, since the phosphorus signal as well as the proton shift of the methyl groups attached to the terphenyl substituent of the starting material, biradical **1**, are strongly high-field shifted upon addition. For all species bearing non-conjugated as well as conjugated multiple bonds, no double addition product was observed when two equivalents of the biradical were used. The reverse reaction, the release of the dienes and diynes was only observed for **1dmb** above 140 °C. The reaction with the cyclic 1,4-cyclohexadiene resulted in a symmetric [2+2] addition. Dehydrogenation within 1,4-cyclohexadiene that should be associated with the formation of benzene was not observed. Finally, dienes and diynes behaved very similarly compared to mono-alkenes and mono-alkynes.

Experimental Section

General: All manipulations were carried out in oxygen- and moisture-free conditions in an argon atmosphere using standard Schlenk or dry-

box techniques. C₆D₆ was dried with Na/benzophenone and freshly distilled prior to use.

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II diffractometer or Bruker D8 quest diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073). The structures were solved by direct methods (SHELXS-97)^[81] and refined by full-matrix least-squares procedures (SHELXL-97).^[82] Semi-empirical absorption corrections were applied (SADABS).^[83] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

NMR Spectroscopy: ¹H, ¹³C{¹H} and ³¹P NMR spectra were recorded with a Bruker AVANCE 250, Bruker AVANCE 300, or a Bruker AVANCE 500. The chemical shifts were referenced to solvent signals (C₆H₆: δ = ¹H = 7.16, ¹³C = 128.0).^[84]

IR Spectroscopy: A Bruker Alpha FT-IR spectrometer with ATR device was used.

Raman Spectroscopy: A LabRAM HR 800 Horiba Jobin Yvon with a High Stability BX40 Microscope (focus 1 μm) and Olympus Mplan 50×NA 0.70 objectives were used. An infrared laser (785 nm, 100 mW, air-cooled diode laser) or a red laser (633 nm, 17mW, HeNe-laser) were used.

CHN Analysis: Analysator vario micro cube from Elementar was used.

Mass Spectrometry A Finnigan MAT 95-XP from Thermo Electron was used.

TGA Measurement TGA analysis was done on a Setaram LapSys 1600-TGA-DSC under argon with a heat rate of 5 K/min. All data were obtained by using the Setsoft 2000 software.

Synthesis of 1dmb: 95 mg (0.13 mmol) [P(μ-Nter)]₂ was dissolved in 4 mL benzene. At room temperature 10.42 mg 2,3-dimethylbutadiene (0.13 mmol) was added with a μL-syringe. The color of the solution turned from orange to yellow after several days. If the reaction was carried out with an excess of 2,3-dimethylbutadiene without benzene as solvent, the reaction was completed after a few minutes. Solvent and remaining 2,3-dimethylbutadiene were removed in vacuo, leading to a yellowish solid. Crystallization attempts were not successful with different solvents and methods. No further purification was necessary. Yield: 104 mg (0.13 mmol, >99%) M(C₅₄H₆₀P₂N₂) = 799 g/mol **¹H NMR** (25 °C, C₆D₆, 500.13 MHz): δ = 0.96 (t, 1 H, P-CH₂, ²J(¹H-³¹P) = 13.09 Hz), 1.1 (d, 3 H, P-C-CH₃, ³J(¹H-³¹P) = 11.05 Hz), 1.5 (dd, 1 H, P-CH₂, ²J(¹H-³¹P) = 13.3, ³J(¹H-³¹P) = 8.4 Hz), 1.64 (s, 3 H, P-C-C-CH₃), 2.0–2.24 (m, 24 H, o-CH₃), 2.3–2.4 (m, 12 H, p-CH₃), 4.61 (s, 1 H, P-C-C-CH₂), 4.70 (s, 1 H, P-C-C-CH₂), 6.58–6.81 (m, 14 H, ArH). **¹³C{¹H} NMR** (25 °C, C₆D₆, 125.77 MHz): δ = 21.4 (s, o-CH₃), 21.5 (s, p-CH₃), 23.6 (d, P-C-C-CH₃, J = 8.03 Hz), 26.6 (d, P-C-CH₃, J = 17.12 Hz), 37.6 (d, P-CH₂, J = 32.9 Hz), 55.3 (d, P-C, J = 30.9 Hz), 111.4 (d, P-C-C-CH₂, J = 11.1 Hz), 148.9 (d, P-C-C, J = 10.0 Hz). **³¹P{¹H} NMR** (25 °C, C₆D₆, 202.48 MHz): δ = 233.6 (d, 1 P, ²J(³¹P-³¹P) = 7 Hz), 230.2 (d, 1 P, ²J(³¹P-³¹P) = 7 Hz). **Raman** (638 nm): $\tilde{\nu}$ = 230 (2), 261 (1), 333 (1), 376 (1), 421 (1), 467 (1), 484 (1), 510 (1), 522 (1), 547 (1), 578 (5), 590 (3), 701 (1), 739 (1), 843 (1), 895 (1), 942 (1), 990 (1), 1003 (1), 1067 (1), 1098 (1), 1163 (1), 1187 (1), 1231 (1), 1282 (2), 1301 (4), 1380 (2), 1409 (2),

1417 (2), 1433 (2), 1483 (1), 1579 (3), 1611 (3), 1626 (1), 2727 (3), 2799 (3), 2815 (3), 2820 (3), 2823 (3), 2829 (3), 2857 (3), 2863 (3), 2876 (3), 2882 (3), 2917 (5), 2938 (3), 2943 (3), 2961 (3), 2964 (3), 2969 (3), 2982 (3), 2985 (3), 2989 (3), 2998 (3), 3005 (3), 3010 (3), 3014 (3), 3023 (3), 3028 (3), 3034 (3), 3041 (3), 3046 (3), 3056 (3), 3061 (3) cm^{-1} . **IR** (ATR): $\tilde{\nu}$ = 435 (w), 456 (m), 472 (w), 488 (w), 503 (m), 550 (m), 575 (w), 594 (w), 622 (w), 645 (w), 670 (w), 690 (m), 705 (w), 746 (s), 791 (s), 806 (m), 816 (m), 843 (vs), 892 (s), 950 (w), 1014 (m), 1031 (m), 1088 (m), 1121 (w), 1171 (w), 1189 (w), 1231 (s), 1268 (w), 1288 (w), 1373 (m), 1402 (s), 1437 (m), 1482 (w), 1579 (w), 1597 (w), 1612 (w), 1626 (vw), 2727 (vw), 2855 (w), 2914 (w), 2945 (w), 2968 (w), 3090 (vw) cm^{-1} . **MS** (CI, pos., isobutane) m/z (%): 83 (100) [dmbH]⁺, 330 (100) [TerNH₃]⁺, 386 (22) [TerNH₂+C₄H₉]⁺, 687 (49) [(TerNH)₂P]⁺, 716 (65) [(TerNP)₂]⁺. **EA** found (calcd.): C 82.00 (81.17), H 8.44 (7.57), N 3.21 (3.51). **Mp**: 140 °C (dec.)

Synthesis of 1dby: At room temperature 88.7 mg (1.12 mmol) [P(μ -NTer)]₂ and 24.7 mg (1.12 mmol) diphenyldiacetylene were combined in a Schlenk flask as solids and dissolved in 3 mL benzene. The solution turned from orange to deep yellow within several hours. Removing the solvent in vacuo lead to an orange/yellowish solid foam. Crystallization attempts were not successful with different solvents and methods. No further purification was necessary. Yield: 112 mg (1.12 mmol, >99%) M(C₆₄H₆₀P₂N₂) = 919 g/mol **¹H NMR** (25 °C, C₆D₆, 500.13 MHz): δ = 1.97 (s, 12 H, *o*-CH₃), 2.15 (s, 12 H, *o*-CH₃), 2.33 (s, 12 H, *p*-CH₃), 6.67 (m), 6.87 (m), 7.15 (m), 7.54 (m), 7.88 (m). **¹³C{¹H} NMR** (25 °C, C₆D₆, 125.77 MHz): δ = 21.2 (s, *o*-CH₃), 21.3 (s, *o*-CH₃), 21.6 (s, *p*-CH₃), 120.1 (s), 129.1 (m), 130.8 (s), 131.6 (s), 136.9 (s). **³¹P{¹H} NMR** (25 °C, C₆D₆, 202.48 MHz): δ = 241.5 (d, 1 P, ²*J*(³¹P-³¹P) = 10.13 Hz), 227.8 (d, 1 P, ²*J*(³¹P-³¹P) = 10.13 Hz). **Raman** (784 nm) $\tilde{\nu}$ = 147 (3), 236 (2), 269 (2), 333 (2), 425 (2), 523 (2), 554 (2), 564 (3), 577 (3), 612 (2), 742 (2), 943 (1), 965 (2), 998 (4), 1021 (2), 1043 (2), 1091 (2), 1176 (3), 1205 (3), 1305 (5), 1382 (7), 1438 (6), 1482 (6), 1534 (5), 1596 (5), 1613 (4), 2165 (1), 2195 (1) cm^{-1} . **IR** (ATR): $\tilde{\nu}$ = 404 (m), 423 (w), 439 (m), 460 (m), 478 (m), 488 (m), 501 (m), 511 (m), 526 (m), 548 (m), 563 (m), 596 (w), 608 (w), 629 (w), 678 (s), 688 (s), 738 (m), 754 (vs), 791 (m), 806 (m), 845 (s), 890 (m), 911 (w), 936 (w), 1029 (m), 1057 (w), 1084 (m), 1158 (w), 1226 (s), 1270 (m), 1299 (w), 1315 (w), 1375 (m), 1406 (s), 1439 (m), 1453 (m), 1480 (w), 1490 (m), 1534 (w), 1575 (w), 1595 (w), 1612 (w), 1719 (vw), 1876 (vw), 2201 (vw), 2315 (vw), 2729 (w), 2789 (w), 2822 (w), 2853 (w), 2871 (w), 2914 (m), 2945 (w), 2962 (w), 2989 (w), 2997 (w). **MS** (CI, pos., isobutane) m/z (%): 330 (21) [TerNH₃]⁺, 386 (5) [TerNH₂+C₄H₉]⁺, 592 (7), 716 (100) [(TerNP)₂]⁺, 919 (43) [M + H]⁺, 975 (14) [M+C₄H₉]⁺. **EA** found (calcd.): C 83.13 (83.63), H 6.73 (6.58), N 2.85 (3.05). **Mp**: 205 °C (dec.)

Synthesis of 1ch4: At room temperature 160 mg (1.21 mmol) [P(μ -NTer)]₂ were dissolved in 1 mL 1,4-cyclohexadiene. The suspension was filtered to remove unsolved solids. The clear solution turned from orange to pale yellow within a few minutes. The product could be obtained as crystals by storing the solution at 5 °C. Yield: 108 mg (1.13 mmol, 61%) M(C₅₄H₅₈P₂N₂) = 797 g/mol **¹H NMR** (25 °C, C₆D₆, 500.13 MHz): δ = 1.22 (m, 2 H, P-CH-CH₂), 2.02 (m, 2 H, P-CH-CH₂), 2.07 (s, 12 H, *p*-CH₃), 2.12 (s, 12 H, *o*-CH₃), 2.13 (m, 2 H, P-CH), 2.33 (d, 12 H, *o*-CH₃, ⁷*J* = 9.5 Hz), 5.77 (m, 2 H, P-CH-CH₂-CH), 6.6–6.74 (m, 6 H, Ter-H), 6.78 (s, 4 H, Mes-H), 6.83 (s, 4 H, Mes-H). **¹³C{¹H} NMR** (25 °C, C₆D₆, 125.77 MHz): δ = 21.1 (s, *o*-CH₃), 21.3 (s, *o*-CH₃), 21.5 (s, 4 C, *p*-CH₃), 22.9 (t, P-CH-CH₂), 38.9 (d, P-CH, ¹*J*(¹³C-³¹P) = 29.5 Hz), 128.7 (s, P-CH-CH₂-CH), 128.8 (s), 131.3 (s), 131.7 (s). **³¹P{¹H} NMR** (25 °C, C₆D₆,

202.48 MHz): δ = 235.2 (s, 2 P). **Raman** (632 nm): $\tilde{\nu}$ = 143 (3), 181 (1), 204 (1), 220 (1), 241 (3), 278 (2), 324 (1), 337 (1), 353 (1), 375 (1), 415 (1), 425 (1), 470 (1), 477 (1), 489 (1), 511 (1), 527 (2), 537 (1), 548 (2), 553 (2), 563 (3), 581 (6), 599 (2), 604 (1), 651 (1), 689 (1), 705 (1), 738 (2), 744 (1), 761 (1), 798 (1), 842 (1), 850 (1), 879 (1), 887 (1), 943 (1), 956 (1), 1005 (1), 1072 (1), 1100 (2), 1157 (1), 1164 (1), 1189 (1), 1208 (1), 1234 (1), 1272 (1), 1284 (3), 1304 (5), 1379 (2), 1385 (2), 1402 (1), 1421 (2), 1436 (2), 1483 (1), 1582 (3), 1613 (3), 1659 (1), 2722 (1), 2731 (1), 2856 (1), 2918 (3), 2946 (1), 2966 (1), 2972 (1), 2976 (1), 2984 (1), 2990 (1), 2994 (1), 3007 (1), 3040 (2) cm^{-1} . **IR** (ATR): $\tilde{\nu}$ = 404 (m), 451 (w), 482 (w), 534 (w), 548 (w), 559 (w), 575 (w), 585 (w), 602 (w), 647 (w), 670 (w), 686 (w), 705 (vw), 732 (w), 742 (w), 759 (m), 791 (m), 810 (w), 841 (vs), 886 (s), 1006 (w), 1016 (w), 1029 (w), 1086 (m), 1099 (w), 1187 (w), 1222 (m), 1261 (w), 1284 (w), 1375 (m), 1400 (s), 1416 (m), 1435 (w), 1482 (w), 1566 (w), 1577 (w), 1610 (w), 1721 (vw), 1874 (vw), 2731 (w), 2846 (w), 2912 (w), 2941 (w), 2993 (w) cm^{-1} . **MS** (CI, pos., isobutane) m/z (%): 79 (6) [C₆H₇]⁺, 716 (100) [(TerNP)₂]⁺, 797 (12) [M + H]⁺, 853 (8) [M+C₄H₉]⁺. **EA** found (calcd.): C 81.21 (81.38), H 7.36 (7.34), N 3.23 (3.51). **Mp**: 215 °C (dec.)

Synthesis of 1od: At room temperature 112.7 mg (1.16 mmol) [P(μ -NTer)]₂ were dissolved in benzene. Octadiene was added in excess. The solution turned from deep orange to pale yellow. After 1 hour the remaining octadiene and solvent were removed in vacuo. Crystallization attempts with benzene, toluene, CH₂Cl₂ were not successful. The formed product was nearly insoluble in benzene, toluene, hexane and CH₂Cl₂. NMR spectroscopy could be done in C₆D₆. And showed two species which could be identified by *R/S* configured isomers. Yield: 128 mg (1.16 mmol, >99%) M(C₅₆H₆₄P₂N₂) = 827 g/mol **¹H NMR** (25 °C, C₆D₆, 500.13 MHz): δ = 0.57–0.69 (m, 1 H, P-CH₂), 0.81–1.12 (m), 1.13–1.31 (m), 1.31–1.45 (m, 1 H, P-CH₂), 1.7–1.81 (m, 1 H, P-CH), 1.94–2.03 (m, 12 H, *p*-CH₃), 2.02 (s, 2 H, P-CH-(CH₂)₃-CH₂), 2.22–2.41 (m, 24 H, *o*-CH₃), 4.93–5.12 (m, 2 H, P-CH-(CH₂)₄-CH-CH₂), 5.69–5.86 (m, 1 H, P-CH-(CH₂)₄-CH), 6.66–6.94 (m, 14 H, ArH). **¹³C{¹H} NMR** (25 °C, C₆D₆, 125.77 MHz): δ = 29.2 (s, CH₂), 33.2 (d, P-CH₂, ¹*J*(¹³C-³¹P) = 32 Hz), 34.3 (s, P-CH-(CH₂)₃-CH₂), 39.3 (dd, P-CH, ¹*J*(¹³C-³¹P) = 40, ²*J*(¹³C-³¹P) = 30 Hz), 114.6 (s, P-CH-(CH₂)₄-CH-CH₂), 139 (s, P-CH-(CH₂)₄-CH). **³¹P{¹H} NMR** (25 °C, C₆D₆, 202.48 MHz): δ = 223.9 (d, 1 P, ²*J*(³¹P-³¹P) = 8 Hz), 224 (d, 1 P, ²*J*(³¹P-³¹P) = 8 Hz), 229.1 (d, 1 P, ²*J*(³¹P-³¹P) = 8 Hz), 229.3 (d, 1 P, ²*J*(³¹P-³¹P) = 8 Hz). **IR** (ATR): $\tilde{\nu}$ = 416 (w), 427 (w), 435 (w), 453 (w), 462 (w), 474 (w), 486 (w), 511 (w), 534 (w), 550 (m), 561 (w), 575 (w), 585 (w), 598 (w), 618 (w), 647 (w), 676 (m), 688 (m), 705 (w), 736 (m), 756 (m), 791 (m), 816 (m), 843 (vs), 895 (m), 946 (w), 956 (w), 1006 (w), 1014 (w), 1031 (m), 1084 (m), 1158 (w), 1187 (w), 1231 (s), 1292 (w), 1375 (m), 1404 (s), 1482 (w), 1579 (w), 1610 (w), 1641 (vw), 1721 (vw), 2729 (vw), 2797 (vw), 2851 (w), 2914 (m), 2945 (w), 2972 (w), 2995 (w), 3034 (w) cm^{-1} . **Raman** (632 nm): $\tilde{\nu}$ = 142 (2), 234 (2), 271 (1), 322 (1), 335 (1), 421 (1), 464 (1), 473 (1), 486 (1), 509 (1), 522 (2), 550 (1), 561 (2), 577 (4), 598 (2), 620 (1), 704 (1), 737 (1), 794 (1), 847 (1), 943 (1), 991 (2), 1003 (2), 1032 (1), 1098 (2), 1107 (1), 1155 (1), 1163 (1), 1187 (1), 1225 (1), 1231 (1), 1237 (1), 1245 (1), 1269 (1), 1284 (2), 1303 (4), 1328 (1), 1376 (2), 1380 (2), 1404 (1), 1422 (2), 1426 (2), 1429 (2), 1432 (2), 1439 (2), 1465 (1), 1481 (1), 1581 (2), 1612 (3), 1642 (1), 2732 (1), 2851 (1), 2856 (1), 2917 (2), 2940 (1), 2946 (1), 3010 (1), 3051 (1) cm^{-1} . **MS** (CI, pos., isobutane) m/z (%): 111 (69) [C₈H₁₅]⁺, 330 (100) [TerNH₃]⁺, 386 (23) [TerNH₂+C₄H₉]⁺, 716 (63) [(TerNP)₂]⁺, 827 (31) [M + H]⁺, 883 (15) [M+C₄H₉]⁺. **EA** found (calcd.): C 81.33 (81.32), H 7.98 (7.80), N 3.32 (3.39). **Mp**: 305 °C (dec.)

Supporting Information (see footnote on the first page of this article): The Supporting Information contains all experimental and computational data as well as all NMR, IR and Raman spectra.

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