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Diels-Alder reactions of 1-phosphabutadienes: A highly selective route to P=C-substituted phosphacyclohexenes

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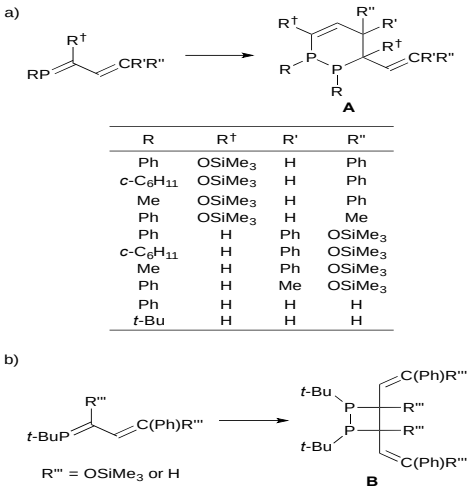
Kinetically stabilized 1-phosphahaloprenes (2-halo-1-phosphabutadienes) as well as 1-phosphaisoprene undergo a hitherto unknown phospha-Diels-Alder dimerization of the P=C–C=C units upon heating. The [4+2] cyclodimerization is highly stereo- and regio-selective. The phosphaalkene-substituted phosphacyclohexene product is an unprecedented P(sp²),P(sp³) ligand that is of interest in polymer/materials science and catalysis.

The replacement of skeletal sp^2 carbon atoms by heavier elements in π-conjugated molecules and polymers has been of considerable recent interest.[1] Heavier congeners of alkenes show many intriguing characteristics, such as lower HOMO-LUMO gap between the frontier orbitals, which have promoted the development of novel functional materials and new ligands for transition metal catalysis.[2,3] 1-Phosphabutadiene (P=C–C=C) is a heavy element-containing π-conjugated system that can be synthesized and isolated by utilizing appropriate stabilization methods for the reactive P=C bond.[4,5] The close analogy between the chemistry of P=C and C=C bonds[6,7] makes these attractive heteroatom-containing building blocks for larger molecules featuring the added functionality of phosphorus. For instance, the isolable 1-phosphaisoprene, Mes*P=C(Me)-CH=CH_2, has recently been polymerized to afford novel polymeric ligands for transition metals.[8]

The Diels-Alder reaction is one of the most important and synthetically useful reactions in organic chemistry.[9] In low-coordinate phosphorus chemistry, an analogous [4+2] reaction of P=C bonds with 1,3-dienes has long been utilized as a chemical trap, thereby proving the existence of fleeting phosphaalkenes (e.g. HP=CH_2).[6,10-12] The Diels-Alder reactions of 1-phosphabutadienes have also been investigated. Interestingly, only one regiochemistry has been reported until now. Namely, the Diels-Alder dimerization of RP=C(R†)–CH=CR'R" gives only the P–P product, diphosphacyclohexene **A** (Fig. 1a).[13,14] Another commonly observed reaction for unhindered P=C bonds is their [2+2] cyclodimerization which has been extended to the head-to-head dimerization of 1-phosphabutadiene giving 1,2-diphosphetane **B** (Fig. 1b).[13,15,16] To date, no dimerization process of the hindered P-Mes*-substituted 1-phosphabutadienes has been reported.



R	R†	R'	R"
Ph	$OSiMe_3$	H	Ph
c-C_6H_{11}	$OSiMe_3$	H	Ph
Me	$OSiMe_3$	H	Ph
Ph	$OSiMe_3$	H	Me
Ph	H	Ph	$OSiMe_3$
c-C_6H_{11}	H	Ph	$OSiMe_3$
Me	H	Ph	$OSiMe_3$
Ph	H	Me	$OSiMe_3$
Ph	H	H	H
t-Bu	H	H	H

Fig. 1 a) Reported [4+2] Diels-Alder dimerization of 1-phosphabutadienes **A**. b) Reported head-to-head [2+2] dimerization of 1-phosphabutadienes **B**.

In this communication, we present an unprecedented phospha-Diels-Alder dimerization of 1-phosphabutadienes, including hitherto unknown halo-functionalized 1-phosphabutadienes. Remarkably, these [4+2] cycloaddition reactions proceed with high diastereo- and regio-selectivity. The resultant P=C-substituted phosphacyclohexenes are shown to be chiral sp^2,sp^3-phosphorus ligands for Pd(II) and are of interest in catalysis and as building blocks for higher-ordered molecules and macromolecules.

Building on the previous studies on palladium(0) catalyzed mono-substitution of gem-dibromophosphaethene [Mes*P=CBr_2],[17] we developed catalytic processes to synthesize halo-functionalized 1-phosphabutadienes **1a** and **1b** as colourless solids (see Supplementary Information).

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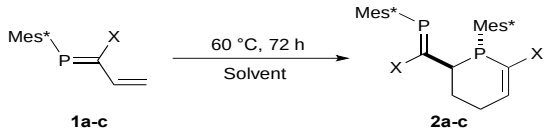
$Pd_2(dba)_3{\cdot}CHCl_3$ in combination with DPEPhos in Et_2O provided a suitable catalyst for the synthesis of 1-phosphabromoprene **1a** from Mes*P=CBr_2 and H_2C=CHMgBr (Table S1). 1-Phosphachloroprene **1b** was prepared from gem-dichlorophosphaethene [Mes*P=CCl_2][18] and H_2C=CHMgBr following a similar catalytic process using $Pd_2(dba)_3{\cdot}CHCl_3$ and dppe.

1-Phosphahaloprenes **1a** and **1b** were employed for thermolysis experiments giving the corresponding novel dimers. 1-Phosphabromoprene **1a** showed evidence for partial dimerization after several days at ambient temperature $CDCl_3$ solutions. Specifically, measurement of the ^{31}P NMR spectrum revealed that the signal assigned to **1a** (δ = 274.9) had been partly consumed and previously unobserved AX signals were detected at 256.6 (d) and –6.5 (d) (J_{PP} = 49 Hz) along with the starting material. In an effort to probe this reactivity, the reaction conditions and solvents were varied to favour the dimeric product **2a** for further characterization (Table S2). By employing the improved conditions (DMF, 0.10 M, 60 °C, 72 h), the phospha-Diels-Alder dimer **2a** was obtained as sole product of the thermolysis of **1a** and was isolated in 63% yield (Scheme 1, Entry 1). Analogous conditions to those used to prepare **2a** were applicable to the [4+2] dimerization of **1b** to afford **2b** in 62% isolated yield (Scheme 1, Entry 2).



1a-c **2a-c**

Entry	Monomer	X	Solvent	Concentration	Yield of **2** / % [a]
1	**1a**	Br	DMF	0.10	63 (63)
2	**1b**	Cl	DMF	0.10	62 (86)
3	**1c**	Me	THF	0.30	50 (80)

[a] Isolated yield. Conversion in parenthesis.

Scheme 1 [4+2] Diels-Alder dimerization of 1-phosphabutadienes **1**.

In order to test the generality of this phospha-Diels-Alder reaction, 1-phosphaisoprene (**1c**)[5,8] was also examined. Specifically, a solution of **1c** in DMF (0.1 M) was heated in a sealed NMR tube to 60 °C and the progress of dimerization was followed by ^{31}P NMR spectroscopy. After 4 d, the signal assigned to monomer (**1c**) had been partially consumed and new doublet resonances were observed 236.7 and –16.4 ppm (J_{PP} = 32 Hz) which are consistent with a dimer **2c**. Unlike that observed for **1a** and **1b**, the conversion of **1c** to **2c** in DMF solution does not exceed 20%. In contrast, heating a THF solution of **1c** (ca. 0.3 M) for 3 d afforded **2c** in 80% conversion. The product was isolated and recrystallized from Et_2O to obtain single crystals of **2c** in 50 % isolated yield (Scheme 1, Entry 3). No retro Diels-Alder process of **2** providing **1** was observed upon heating in DMF (**2a**) or in THF (**2c**).

Crystals of **2a** and **2c** were obtained from a 1:1 mixture of chloroform and ethanol at 25 °C or by cooling a concentrated diethyl ether solution to –40 °C, respectively. Analysis of the crystals by X-ray crystallography revealed that both products were unprecedented [4+2] cyclodimers which are shown in Fig. 2. The 6-membered phospha-cyclohex-2-ene ring shows a typical half-chair structure. Interestingly, the chiral centres at C6 and P2 are formed diastereoselectively and thus, the H-atom at C6 and the P2 lone pair have *trans* disposition in the crystal structures. This is consistent with the observation of a single set of signals in the ^{31}P NMR spectra of **2a** and **2c**. In addition to being highly stereoselective, it is noteworthy that the dimerization of **1a** and **1c** are both head-to-tail and the products (**2a** and **2c**) each possess a reactive exocyclic P=C double bond. The P1–C1 distances of 1.685(7) Å (in **2a**) and 1.682(2)/1.683(2) Å (in **2c**) are typical of $\lambda^3\sigma^2$-P=C double bonds.[6]

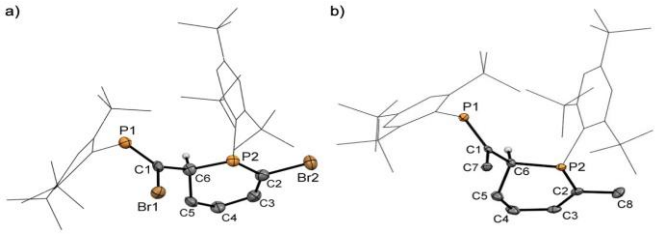


Fig. 2 a) Molecular structure of **2a** (50% probability level). For clarity, Mes* groups are shown as capped sticks and hydrogen atoms except for the CH group are omitted. Selected bond lengths (Å): P1–C1 1.685(7), C1–Br1 1.904(6), P2–C2 1.818(6), P2–C6 1.868(7), C1–C6 1.534(8), C2–Br2 1.914(6), C2–C3 1.35(1), C3–C4 1.49(1), C4–C5 1.55(1), C5–C6 1.556(9). b) Molecular structure of **2c** (Molecule 1 of 2; 50% probability level). Hydrogen atoms except for the CH group are omitted for clarity. Selected bond lengths (Å): Molecule 1: P1–C1 1.683(2), C1-C7 1.509(2), P2–C2 1.836(2), P2–C6 1.873(2), C1–C6 1.521(2), C2–C8 1.510(2), C2–C3 1.331(3), C3–C4 1.500(3), C4–C5 1.524(3), C5–C6 1.545(2); Molecule 2: P1–C1 1.682(2), C1-C7 1.506(2), P2–C2 1.854(2), P2–C6 1.873(2), C1–C6 1.515(2), C2–C8 1.513(3), C2–C3 1.328(3), C3–C4 1.495(3), C4–C5 1.520(3), C5–C6 1.556(2).

To gain insight into the mechanism of these unprecedented [4+2] cycloaddition reactions of 1-phosphabutadienes, DFT calculations were undertaken. Two types of [4+2] Diels-Alder dimerization are possible between a P=C-C=C moiety and the C=C of another P=C-C=C unit. Based on the crystallographic and spectroscopic data, the dimerization of **1a** and **1c** gives only **Type I** products (i.e. **2a** and **2c**, respectively, Fig. 3a) with no evidence of **Type II** products (Fig. 3b). Although the structure of **2b** was not analyzed by X-ray crystallography, ^{31}P NMR spectroscopy is also consistent with an analogous highly regioselective dimerization mechanism. The **Type I** and **Type II** dimerization mechanisms were each modelled using DFT. The optimized transition state of the **Type I** dimerization of **1a** (Fig. 3a) suggests almost no second-order interaction due to steric repulsion, and in fact the **Type I** *endo* product of **1** could not be obtained at all. The transition state was checked by Intrinsic Reaction Coordinate (IRC) calculations, and the activation parameters were determined at the ωB97XD/6-311G(d,p) level[19,20] [$\Delta H^{\ddagger}$,$\Delta G^{\ddagger}$ (kcal/mol): 9.1, 25.8 (**1a**); 10.7, 27.7 (**1c**)]. Similar modeling of the transition state for the **Type II** *endo* mechanism (Fig. 3b) revealed a higher activation energy [$\Delta H^{\ddagger}$,$\Delta G^{\ddagger}$ (kcal/mol): 13.2, 29.3 (**1a**); 13.7, 29.9 (**1c**)]. The **Type**

II *exo* pathway reveals higher activation energies [$\Delta H^{\ddagger}$,$\Delta G^{\ddagger}$ (kcal/mol): 16.0, 31.6 (**1a**); 15.4, 30.5 (**1c**)] (Figs. S1-3, S5-7).

Likely, these differences are primarily a consequence of steric effects. For instance, Fig. 3 shows that the **Type I** transition state permits close contact between the unhindered $=CH_2$ moieties (i.e. C4 and C5) whereas the **Type II** *endo* transition state necessitates a less favourable C4 to C6 approach. In contrast, the approach of P2 to C6 in the **Type I** transition state appears to be slightly less favourable than the approach of P2 to C5 in the **Type II** *endo* transition state. We speculate that these steric effects play a large role in the high regioselectivity of the [4+2] cycloaddition of Mes*-substituted 1-phosphabutadienes **1.** Likewise, the dimerization of mesityl-substituted 1-phosphabromoprene, Mes-P=C(Br)-CH=CH_2, shows a similar, albeit lower activation energy, preference for the **Type I** mechanism [$\Delta H^{\ddagger}$,$\Delta G^{\ddagger}$ (kcal/mol): 6.6, 23.8 (Type I); 8.9, 25.9 (Type II, *endo*), 9.2, 25.2 (Type II, *exo*) (Figs. S8-S10). The importance of steric effects in the reaction mechanism is supported by the fact that the analogous calculations for the unknown 1-phosphabromoprene, Ph-P=C(Br)-CH=CH_2, showed that the **Type II** *endo* pathway has the lowest activation energy [[$\Delta H^{\ddagger}$,$\Delta G^{\ddagger}$ (kcal/mol): 7.5, 20.2 (Type I); 6.1, 19.0 (Type II, *endo*), 7.0, 18.2 (Type II, *exo*)] (Figs. S11-13). We conclude that the hitherto unknown selectivity of the P=C-C=C unit as enophile and the C=C bond of a second molecule as dienophile affording the [4+2] dimer **2** results from the sterically encumbered substituent.[21]

To assess the potential utility of these novel P(sp^2),P(sp^3) hybrids as chelating ligands for transition metals, a solution of **2c** in dichloromethane was treated with Pd(cod)Cl_2. The reaction progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and revealed that the signals assigned to **2c** [δ 236.7 (d), –16.4 (d), $^3J_{PP}$ = 31 Hz] were consumed over several hours and were replaced by doublet resonances at 212.1 and 62.6 ppm ($^2J_{PP}$ = 18 Hz) indicative of the formation of complex **2c**·PdCl_2. This formulation was confirmed from the X-ray crystallographic analysis of crystals obtained by slow evaporation of the solvent (Fig. 4). The metrical parameters are as expected for such a complex.

In summary, we have described the hitherto unknown [4+2] dimerization of 1-phosphabutadienes **1a-c** bearing the sterically encumbering Mes* group as the P-substituent. The newly characterized Diels-Alder dimers **2a-c** are formed in a highly regio- and diastereo-selective **Type I** [4+2] cycloaddition. The chiral P=C-substituted phosphacyclohexenes **2a-c** are attractive additions to the limited set of known sp^2,sp^3-hybridized P,P-chelate ligands[22] and are of potential utility in transition metal-catalysis. Also, a subject of future study will be the polymerization chemistry of the new P-analogues of bromoprene and chloroprene (**1a** and **1b**) as well as the functional dimers (**2a-c**).

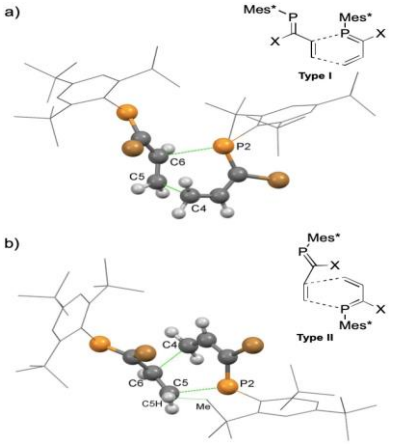


Fig. 3 a) DFT-optimized transition state for **Type I** affording **2a** (X = Br) [ωB97XD/6-311G(d,p)]. Distances C4–C5 and P2–C6 are 2.021 and 2.981 Å, respectively. b) DFT-optimized transition state for **Type II** affording *endo* product [ωB97XD/6-311G(d,p)]. Distances C4–C6 and P2–C5 are 2.235 and 2.475 Å, respectively. A close contact between the C5H hydrogen and the Me group in one of the *o*-*t*-butyl group is shown (C5H–Me: 2.649 Å).

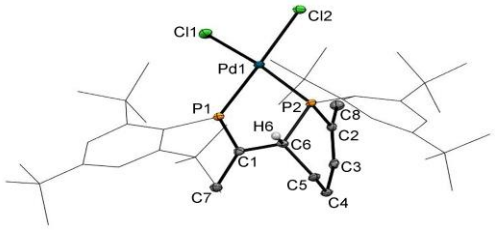


Fig. 4 Molecular structure of **2c**·PdCl_2 (50% probability level). For clarity, Mes* groups are shown as capped sticks and hydrogen atoms except for the CH group are omitted. Solvents of crystallization (2 x CH_2Cl_2) are not shown. Selected bond lengths (Å): P1–Pd1 2.2360(7), P2–Pd1 2.2816(7), Cl1–Pd1 2.3637(7), Cl2–Pd 2.3340(7), P1–C1 1.671(3), C1-C7 1.502(4), P2–C2 1.834(3), P2–C6 1.870(3), C1–C6 1.507(4), C2–C8 1.517(4), C2–C3 1.335(4), C3–C4 1.499(4), C4–C5 1.516(4), C5–C6 1.542(4).

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Conflicts of interest

There are no conflicts to declare.

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