Azavinylidenephosphoranes: a new class of cyclic push-pull carbenes

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Dedication ((optional))

Abstract: The synthesis of a novel family of cyclic push-pull carbenes, namely azavinylidene phosphoranes is described. The methodology is based on a formal [3+2] cycloaddition between terminal alkynes and phosphine-imines followed by an oxidation / deprotonation step. Carbenes **6**, obtained by simple deprotonation, exhibit typical transient carbene reactivity like intramolecular C-H insertion reaction and a pronounced ambiphilic character exemplified by [2+1] cycloaddition with electron poor methyl acrylate. Due to the cyclic structure, carbenes **6** also exhibit an excellent

coordination ability toward transition metals. Rh(I)-complex **10** was obtained in excellent yield and fully characterised by multinuclear NMR spectroscopy and X-ray crystallography. The corresponding Rh(I)-carbonyl complex was also prepared indicating that carbenes **6** belong to the strongest σ -donating ligands to date. DFT calculations confirmed the high σ -donation ability of **6** and their classification as push-pull carbenes with a relatively small singlet-triplet energy gap of (23.2 - 24.3 kcal.mol⁻¹).

Introduction

Since the isolation of the first stable carbenes in the late 80s,^[1] carbene chemistry has become a very active research field.^[2] The development of various stabilization modes afforded many useful tools like synthetic reagents,^[3] organocatalysts^[4] or ligands for transition metals in homogenous catalysis.^[5] The success in this latest application is mainly due to the peculiar properties of N-heterocyclic carbenes (NHCs).^[6] Indeed, their strong σ -donor character and their excellent ability to bind metals afford not only

robust but also very efficient organometallic catalysts.^[7] Interestingly, Bertrand offered new possibilities for structure modifications around the carbenic centre with the substitution of one amino group of NHCs by a sp³-hybridized carbon yielding to cyclic alkyl(amino)carbenes (CAACs),^[8] which are stronger σ -donating ligands than NHCs. Closely related, in 2008, Kawashima, Fürstner and Bertrand independently reported the synthesis of carbenes bearing an exocyclic ylide function adjacent from the carbene centre, namely the amino(ylidic)carbenes (N-YHCs),^[9] which are also excellent donor ligands. Moreover, CAACs present an extraordinary rich chemistry such as small molecules activation (H₂, NH₃, CO, P₄),^[10] and the corresponding transition metal complexes demonstrated very original catalytic properties (such as α -arylation of ketones and aldehydes with aryl chlorides at room temperature, coupling enamines with terminal alkynes to yield allenes with loss of imines or hydroamination of alkynes and allenes with ammonia).^[11] These properties are the result of the particular structure of CAACs but also the consequence of a considerably reduced singlet-triplet energy gap (45.1 kcal.mol⁻¹) when compared with NHCs (~80 kcal.mol⁻¹).^[12] There are only few examples of stable cyclic carbenes presenting a high electrophilic character. We can cite diamidocarbenes (DACs) showing an atypical NHC reactivity such as C-H insertion, reversible coupling with carbon monoxide, and cyclopropanation reactions with a broad range of olefins.^[13] The original N-Heterocyclic carbene (N_{pyr}HC), featuring a bridgehead nitrogen atom, also shows interesting electrophilic properties especially as ligand for gold complexes, which are active catalysts in hydroamination of alkynes and allenes with hydrazine.^[14] Finally carbenes bearing an intracyclic ylide function, known as cyclic vinylidenephosphoranes (CVPs) also display strong electron-donating abilities and small S/T energy gap, however, up to now, their development was limited because of restricted synthesis (Scheme 1).^[15]

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Scheme 1. Stable carbenes.

The peculiar structure of CVPs has retained our attention. Indeed, CVPs are cyclic heteroallenes containing a PC-yldic bond and a CC-double bond, which can be formally described as cyclic push-pull carbenes (III) (Scheme 2).

Scheme 2. Mesomeric structures of cyclic vinylidenephosphoranes.

Structural study revealed that the yldic π -bond is extremely polarized due to a very weak interaction between the carbene lone pair and the phosphonio group (III).^[15b] As a consequence, the carbene lone pair is fully available for coordination to transition metals, explaining why this cyclic carbene was found to be a strongly nucleophilic ligand. In addition, because of the substitution pattern of CVPs, this carbene presents a considerably reduced S/T energy gap (32.4 kcal.mol⁻¹).^[15b] Similarly to the case of Enders' carbene,^[16] the introduction of a phosphazene fragment at the backbone, instead of the ylide function, should further increase the ambiphilic character of a new family of carbenes the cyclic azavinylidenephosphoranes (CAVPs).

As a part of our research program towards new push-pull carbenes,^[17] herein, we report the synthesis, reactivity, and ligand properties of the first examples of cyclic azavinylidenephosphoranes (CAVPs) (Scheme 3).

Scheme 3. Mesomeric structures of cyclic azavinylidenephosphoranes.

Results and Discussion

Synthesis

With this framework in mind, we designed a general synthetic approach to cyclic azavinylidenephosphoranes. Our methodology, inspired by seminal results of Zeiss,^[18] is based on a formal [3+2] cycloaddition between phosphine-imine **1** and terminal alkynes **2** to afford five-membered cyclic phosphazenes **4**. An oxidation/deprotonation step using CBr₄ gives the phosphonium salts **5**, which are the precursors of CAVPs (Scheme 4). The easy modification of phosphine-imine **1** substituents or / and acetylenic derivatives **2** should allow an easy modulation of the steric and electronic properties of the corresponding carbenes.

Scheme 4. Synthetic approach.

The study was initiated with phosphine-imine **1** bearing bis(diisopropylamino) groups on the phosphorus atom that will further bring an efficient kinetic stabilization of the carbenic centre. Three types of the acetylenic derivatives **2a-c** were considered to balance the electrodeficiency of the carbenic centre by electronic or steric effects. The reaction is very substrate dependent, and can be performed at room temperature with an activated alkyne (**2a**) whereas xylene reflux is needed in the case of phenylacetylene (**2b**), and no reaction was observed in the case of mesitylacetylene (**2c**), even under drastic conditions, probably for steric reasons. The first formed phosphazenes **3** (observed by ³¹P NMR in the case of **3a**) rearrange to the thermodynamically more stable phosphazenes **4**, via a 1,3-proton shift. Derivatives **4a** and **4b** were isolated in good yields 82 % and 57 % respectively, and fully characterized by multinuclear NMR spectroscopy. Selected spectroscopic data, in good agreement with previously described similar heterocycles, can be found in Table 1.^[19]

Table 1. Selected spectroscopic data for **4**, **5** and **6** [Chemical shifts in ppm (coupling constants in Hertz)].

	4	5	6
P(¹ H)	4a 74.6 4b 72.6	5a 69.7 5b 66.3	6a 103.5 6b 95.8
¹ H	4a 2.99 (10.4 Hz) 4b 3.08 (10.5 Hz)	5a 9.81 (28.9 Hz) 5b 8.83 (30.6 Hz)	-
¹³ C	4a 31.5 (68.5 Hz) 4b 36.4 (69.5 Hz)	5a 141.8 (93.9 Hz) 5b 134.7 (101.8 Hz)	- 6b 234.4 (93.6 Hz)

The oxidation-deprotonation sequence of phosphazenes **4** can be performed either in one step with CBr₄ or in two steps using Br₂ as oxidant then NEt₃ / *t*BuOK as base. Phosphonium salts **5a** and **5b** display single resonances (δ = 69.7 and δ = 66.3 ppm) in ³¹P NMR spectroscopy, and the characteristic ethylenic protons

appear as doublets at low field in the ^1H NMR spectra ($\delta = 9.81$ ppm, $^2J_{\text{HP}} = 28.9$ Hz and $\delta = 8.83$ ppm, $^2J_{\text{HP}} = 30.6$ Hz). In order to optimize the purification step and to obtain suitable crystals for an X-Ray diffraction analysis, anion metathesis was quantitatively performed with Me_3SiOTf (Scheme 4). Both compounds **5'a,b**, were obtained as colorless crystals from saturated solutions of CH_2Cl_2 / Et_2O or CH_2Cl_2 / THF, respectively, and the structures were confirmed by X-ray diffraction analysis (Figure 1 and 2).

Figure 1. Molecular structure of phosphonium salt **5'a**. Thermal ellipsoids were set at 30 % probability. Hydrogen atoms, except the one on the 5-membered ring, and TfO^- were omitted for clarity; selected bond lengths [Å] and angles [°]: P1-N1: 1.690(2); P1-C1: 1.800(3); N1-C3: 1.302(4); C1-C2: 1.330(4); C2-C3: 1.516(4); C2-C4: 1.498(4); C3-C6: 1.468(4); P1-N2: 1.612(2); P1-N3: 1.616(2); C2-C1-P1: 105.9(2); N1-P1-C1: 96.45(12); C1-C2-C3: 112.9(2); N1-C3-C2: 115.8(2); C3-N1-P1: 108.61(19).

Figure 2. Molecular structure of phosphonium salt **5'b**. Thermal ellipsoids were set at 30 % probability. Hydrogen atoms, except the one on the 5-membered ring, and TfO^- were omitted for clarity; selected bond lengths [Å] and angles [°]: P1-N1: 1.669(4); P1-C1: 1.778(5); N1-C3: 1.317(7); C1-C2: 1.342(7); C2-C3: 1.511(7); P1-N2: 1.611(4); P1-N3: 1.618(4); C2-C1-P1: 107.4(4); N1-P1-C1: 96.6(2); C1-C2-C3: 110.7(4); N1-C3-C2: 115.9(5); C3-N1-P1: 108.4(3).

Similarly to the previously described conjugated acid of **CVP1** (cf Table 2), cyclic phosphonium salts **5'a,b** show significant localized diene character with C1C2 and C3N1 bonds which are typically short, respectively 1.342(7) and 1.317(7) Å, whereas C2C3 bond length are in the range expected for a single bond.^[15b]

Scheme 5. Deprotonation of phosphonium salt **5'a,b**.

Deprotonation of **5'** was carried out in THF at low temperature (-80 °C) using non nucleophilic strong bases such as potassium hexamethyldisilazane (KHMDs) or mesityl lithium (Scheme 5).^[20] The formation the desired azavinylidenephosphoranes **6a** and **6b** was indicated in ^{31}P NMR spectroscopy by single resonances respectively at $\delta = 103.5$ ppm and $\delta = 95.8$ ppm, reminiscent of the phosphorus chemical shift observed for **CVP1** ($\delta = 86.4$ ppm in C_6D_6).^[15b] Variable-temperature multinuclear NMR studies indicated that **6a** was unstable and decomposed at low temperature (-80 °C). However, **6b** is perfectly stable at low temperature ($T < -15$ °C), and it can be fully

characterized by NMR spectroscopy. Of special interest, the characteristic ^{13}C NMR signal of the carbenic center appears as a low field doublet at $\delta = 234.4$ ppm ($^1J_{\text{CP}} = 96.3$ Hz), in the typical area of NHC carbenic centres. Unfortunately, all our attempts to crystallize **6b** were unsuccessful.

Calculations

In order to get a better insight into the structure and electronic nature of CAVPs, theoretical calculations have been performed. We have optimized the geometries of the phosphonium salts **5'b**, and carbene **6b** at the B3LYP level of calculation. The results obtained for **5'b** are in excellent agreement with the experimental values shown in Figure 2, with mean absolute deviations of 0.014 Å for interatomic distances and 0.4 ° for bond angles.^[21] According to the NBO method, the Lewis structure which gives the best description of the electronic structure of **6** is **II** (Scheme 3).^[21] Figure 3 shows the HOMO and LUMO of **6b**. The HOMO is localized on the carbenic center whereas the LUMO corresponds to the delocalized π -system. The energy level of the HOMO and the singlet-triplet energy gap were calculated for different CAVPs and CVPs (Table 2). The values obtained for the HOMO level of **6a-d** are high, all these carbenes are more nucleophilic than NHCs. As expected, the HOMO levels of CAVPs are directly influenced by the inductive effect of R' group. In contrast, the S/T energy gap calculated for carbenes **6a-d** are very similar (~ 24 kcal.mol $^{-1}$), much smaller than the value reported for the previously described **CVP1**.^[15b] In order to understand the origin of this difference, we calculated the S/T energy gap of other CAVPs and CVPs. Comparing values obtained for **CAVP1** and **CVP2,3**, it appears than both the nitrogen atom and the phenyl group at the backbone are needed to obtain a carbene showing a pronounced ambiphilic character.

Figure 3. HOMO (left) and LUMO (right) of **6b** (± 0.05 contours) computed at the B3LYP/6-31G(d) level of calculation.

Table 2. Calculated HOMO energy (E_H , in eV), singlet-triplet energy gap (ΔE_{ST} , in kcal.mol⁻¹), electrophilicity (ω , in eV) and maximum saturation electronic charge (ΔN_{max} , in a. u.), for various cyclic CAVPs and CVPs at the B3LYP/6-31G(d) level of calculation.

	R'	E_{HOMO}	ΔE_{ST}	ω	ΔN_{max}
	CO ₂ Me	- 5.03	23.2	1.82	1.07
	Ph	- 4.83	24.3	1.65	1.03
	Mes	- 4.77	22.7	1.67	1.04
	Me	- 4.70	23.7	1.48	0.95
		- 5.01	26.2	1.53	0.94
		- 4.40	32.4	0.91	0.71
		- 4.70	27.9	1.23	0.84
		- 4.58	25.5	1.34	0.92

We have also computed the electrophilicity ω and the maximum saturation electronic charge ΔN_{max} of each carbenic species **6a-d**, **CAVP1** and **CVP1-3** (Table 2). The latter magnitude ΔN_{max} is closely related to the number of electrons required to complete the octet of compounds gathered in Table 2. Thus, for an ideal carbene with non-interacting groups one would expect an approximate value ΔN_{max} of ≈ 2.0 . In singlet C_{2v} -symmetric carbenes CH_2 and CCl_2 the computed values are 1.50 and 1.43 a. u., the corresponding electrophilicities being 3.68 and 3.88 eV, respectively.^[22] Our results for compounds **CVP1** and **CVP2** show quite low ω and ΔN_{max} values because of the efficient electron-releasing effect on the carbene moiety of the fused bicyclic ring and phenyl groups. Moreover, carbene **6a** which combines a nitrogen atom at the backbone and an electron-withdrawing ester function exhibits the highest ω and ΔN_{max} values (Table 2), in good agreement with its experimentally observed high reactivity (vide infra). Carbenes **6b,c**, which incorporate two vicinal non-coplanar aryl groups in the 1,2,5-azaphosphole ring, represent a good compromise between relative stability and reactivity, with ΔN_{max} value of ca. 1 a. u.

Carbenic properties

The reactivity of stabilized carbenes depends on the singlet-triplet energy gap, and carbene **6b** presenting a relatively small S/T gap of 24.3 kcal.mol⁻¹ should exhibit an ambiphilic character and the reactivity of transient singlet carbenes.

The stability of carbenes **6** is strongly dependent on the nature of substituents. Indeed, **6a** ($R' = CO_2Me$) decomposes at low temperature giving a complex mixture of products, whereas, **6b** ($R' = Ph$) is stable for days at $T < -15^\circ C$. By increasing slowly the temperature to rt, carbene **6b** undergoes a clean C-H insertion, involving the phosphorus isopropyl substituent, affording the fused bi-cyclic structure **7** (Scheme 6). Phosphazene **7** was isolated as a colorless oil and fully characterized by multinuclear NMR spectroscopy. A single resonance at $\delta = 66.6$ ppm is observed in the ³¹P NMR spectrum. In the ¹H NMR spectrum, the inserted hydrogen atom appears as a doublet signal at $\delta = 3.37$ ppm ($^2J_{HP} = 12.0$ Hz), and the corresponding carbon atom resonates at $\delta = 61.9$ ppm as a doublet with a large coupling constant ($^1J_{CP} = 54.7$ Hz) in the ¹³C NMR spectrum. The bicyclic structure could be

confirmed by 2D HMBC experiments showing a strong ³J heteronuclear chemical shift correlation between the carbon alpha to the phosphorus and the two methyl groups of the four-membered ring. ¹³C NMR data are in good agreement with azaphosphetanes previously described in the literature.^[23]

Usually alkenes react with singlet carbenes in a concerted fashion to give the corresponding cyclopropane products.^[2b] In the case of carbene **6b** a clean reaction was observed with an electron poor olefin, methyl acrylate, at $-80^\circ C$, affording the corresponding cyclopropane **8** (Scheme 6). Since the spiro phosphazene **8** slowly decomposes at room temperature, it was characterized by multinuclear NMR spectroscopy at low temperature.

Scheme 6. Reactivity of carbene **6b**: C-H insertion and cyclopropanation reactions.

A single resonance, in the ³¹P NMR spectrum at $\delta = 75.7$ ppm indicates a diastereoselective cyclopropanation reaction. The spiranic carbon atom resonates as a doublet at $\delta = 37.3$ ppm in the ¹³C NMR spectrum with a large coupling constant ($^1J_{CP} = 96.7$ Hz) indicative of a direct PC-connectivity. In addition the other two three-membered ring carbon atoms CH_2 and CH , appear also as doublets at $\delta = 22.3$ ($^2J_{CP} = 2.8$ Hz) and $\delta = 26.6$ ($^2J_{CP} = 7.2$ Hz), respectively. In the ¹H NMR spectrum the diastereotopic methylene protons give a multiplet at $\delta = 1.42$ ppm and a doublet of doublets at $\delta = 1.89$ ppm ($^2J_{HH} = 4.0$ Hz, $^3J_{HH} = 6.4$ Hz, $^3J_{HP} = 13.0$ Hz). The alpha proton of the ester function is located at $\delta = 2.10$ ppm (ddd, $^3J_{HH} = 5.6$ Hz, $^3J_{HH} = 6.4$ Hz, $^3J_{HP} = 7.6$ Hz). Finally, the spiranic structure is clearly confirmed by 2D HMBC experiments showing a strong heteronuclear chemical shift correlation between the 3-membered ring protons and the quaternary carbon alpha to the phosphorus atom. The instability of **8** is mainly due to the presence of the phosphazene function, which presents a strong nucleophilic character. Indeed, the addition of one equivalent of MeOTf, at low temperature, smoothly affords the air stable spiro phosphonium salts **9**, which presents very similar NMR data to those of **8** (Scheme 6).

Ligand properties

Despite its thermal instability carbene **6b** appears to be an efficient new ligand for transition metals. Indeed, mixing its precursor **5'b**, KHMDS, and $[RhCl(COD)]_2$ at $-80^\circ C$, leads to the corresponding Rh(I)-complex **10**, in 71% yield, as a thermally and air stable red solid (M. P. $159 - 161^\circ C$) (Scheme 7). In ³¹P NMR, a signal at $\delta = 80.9$ ppm appears as a doublet with a small Rh-P-coupling constant ($^1J_{PRh} = 6.2$ Hz). The formation of complex **10** can clearly be ascertained by ¹³C NMR where the carbene center

moves upfield, as is typical for this type of metal complexes, to $\delta = 195.8$ ppm (dd, $^1J_{CP} = 41.2$ Hz and $^1J_{CRh} = 7.6$ Hz) confirming the direct connectivity between carbon and rhodium atoms. The structure of **10** was unambiguously established by an X-ray diffraction analysis (Figure 4). The P1C1C2 angle in **10** (101.1°) is slightly narrower than the azavinylidenephosphorane precursor **5'b** (107.4°). The rhodium-carbon bond length is typical for a single bond (2.050 Å), in the range of previously reported rhodium complexes (1.94 – 2.10 Å).^[5b]

Scheme 7. Synthesis of Rh(I)-complex **10**.

Figure 4. Molecular representation of rhodium complex **10**. Thermal ellipsoids were set at 30 % probability. Hydrogen atoms were omitted for clarity; selected bond lengths [Å] and angles [$^\circ$]: Rh1-C1: $2.050(2)$; C1-C2: $1.364(3)$; C2-C3: $1.499(3)$; C3-C4: $1.486(3)$; C2-C10: $1.484(3)$; Rh1-Cl1: $2.3999(1)$; P1-N2: $1.632(2)$; N1-C3: $1.301(3)$; P1-C1: $1.823(2)$; P1-N3: $1.638(2)$; P1-N1: $1.688(2)$; C1-Rh1-Cl1: $95.24(5)$; N2-P1-N3: $109.16(9)$; N1-P1-C1: $99.67(9)$; C3-N1-P1: $105.97(13)$; C2-C1-P1: $101.11(14)$; C2-C1-Rh1: $127.45(15)$; P1-C1-Rh1: $130.96(11)$; C1-C2-C3: $115.37(17)$; C10-C2-C3: $120.14(17)$; N1-C3-C2: $117.41(17)$.

The carbonyl stretching frequencies of *cis*-[RhCl(CO)₂L] complexes are recognized to give an excellent measure of the σ -donor vs π -acceptor properties of ligand L.^[24] The corresponding Rh-dicarbonyl complex **11** was easily prepared by bubbling carbon monoxide through a dichloromethane solution of **10** (Scheme 8). Monitoring the transformation by ^{31}P NMR spectroscopy, the gradual consumption of **10** with the concomitant formation of **11** was observed. Complex **11** exhibits a signal at $\delta = 84.6$ ppm as a doublet ($^2J_{PRh} = 6.7$ Hz) in ^{31}P NMR spectrum. The chelating carbon appears at $\delta = 177.9$ ppm as a doublet of doublets ($^1J_{CP} = 35.8$ Hz and $^1J_{CRh} = 23.6$ Hz) in the ^{13}C NMR spectrum. In addition, two characteristic resonances were observed for the two carbonyl groups at $\delta = 183.5$ ppm (d, $^1J_{CRh} = 74.2$ Hz) and $\delta = 185.4$ ppm

(dd, $^3J_{CP} = 10.4$ Hz and $^1J_{CRh} = 52.5$ Hz). The infrared spectrum shows the characteristic CO stretching frequencies with an average value of 2028 cm^{-1} . This value highlights the strong σ -donation ability of **6b**, which is much stronger than NHCs, but remaining weaker than **CVP1** probably because of the higher electrophilic character of **6b** (Scheme 9). Computed scaled average carbonyl stretching frequencies for **11** was found to be 2025 cm^{-1} , in excellent agreement with experimental values (see Scheme 9). The geometry of the complex of **CVP1** with Rh(CO)₂Cl was also optimized and the computed average CO stretching is 2018 cm^{-1} . Finally, the electron donor character of **6b** is also reflected in the natural atomic population analysis of complexes **10** and **11** which shows that the charge transferred from **6b** to the metal fragment are 0.40 a.u. (**10**) and 0.46 a.u. (**11**).

Scheme 8. Synthesis of Rh(I)-complex **11**.

Scheme 9. Comparison of average IR band of $\nu(\text{CO})$ in *cis*-[RhCl(CO)₂L].^[8, 15b, 25]

Conclusion

We established an efficient new methodology to access to cyclic azavinylidenephosphoranes in three steps. The first example **6b** was fully characterized by multinuclear NMR spectroscopy, and its chemical reactivity highlight a strong ambiphilic character exemplified by C-H insertion or cyclopropanation reactions with electron-poor alkenes. This chemical behavior is in good agreement with calculations which predict a small S/T energy gap for this new family of carbenes. These cyclic push-pull carbenes also show an excellent ability to bind transition metal and their high σ -donor aptitude was established by analysis of IR-CO stretching frequencies of the corresponding Rh(I)-carbonyl complexes **11**. In addition, the use of these carbenes as ligand in asymmetric catalysis can be easily envisaged because of the presence of a potentially P-chiral centre adjacent to the carbenic centre that bring the chiral information as close as possible to the metallic centre and therefore hopefully lead to high stereoselection. Development of new models using this methodology to increase their thermal stability is under active investigation.

Experimental Section

General procedures

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry and oxygen-free solvents were used. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 400 or Avance 300

spectrometers. ^1H NMR and ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical are expressed in ppm relative to 85 % H_3PO_4 . IR spectra were recorded on a Varian 640-IR. Mass spectra were recorded on Hewlett Packard 5989A spectrometer.

Cyclic phosphazene 4b: Bis(diisopropylamino)phosphine imine **1** (16.7 g, 49.9 mmol) was dissolved in 40 mL of xylene, and heated to reflux. Then a solution of phenylacetylene **2b** (6.6 mL, 60.1 mmol) in xylene (10 mL) was added drop by drop by the top of the condenser. The mixture is heated for 24h. Then a new addition of a solution of phenylacetylene (3.0 mL, 27.4 mmol) in xylene (5 mL) is done and reflux is extended for 24h. All the volatiles were removed under vacuum. Extraction of phosphazene **4b** with pentane (3 x 20 mL) is performed. Evaporation of solvent to obtain a saturated solution of pentane is realized and precipitation occurs at -30°C . Phosphazene **4b** is obtained as a brownish powder (12.4 g, 57 % yield). M.p. = $105\text{--}107^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, CDCl_3): $\delta = 72.6$; ^1H NMR (300.1 MHz, 298 K, CDCl_3): $\delta = 1.28$ (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 1.34 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, NCHCH_3), 3.08 (d, $^2J_{\text{HP}} = 10.5$ Hz, 2H, PCH_2), 3.73 (sept. d, $^3J_{\text{HH}} = 6.9$ Hz, $^3J_{\text{HP}} = 13.8$ Hz, 4H, NCHCH_3), 6.82–6.83 (m, 3H, CH_{Ar}), 6.99–7.01 (m, 2H, CH_{Ar}), 7.20–7.25 (m, 3H, CH_{Ar}), 7.37–7.41 (m, 2H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, CDCl_3): $\delta = 23.1$ (s, NCHCH_3), 23.3 (s, NCHCH_3), 36.4 (d, $^1J_{\text{CP}} = 69.5$ Hz, PCH_2), 46.2 (s, NCHCH_3), 103.4 (d, $^2J_{\text{CP}} = 22.3$ Hz, $\text{NC}=\text{C}$), 121.8 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 140.3 (d, $^3J_{\text{CP}} = 16.3$ Hz, C_{ipso}), 142.2 (d, $^2J_{\text{CP}} = 28.2$ Hz, C_{ipso}), 157.7 (d, $^2J_{\text{CP}} = 12.1$ Hz, $\text{N}=\text{C}$); HRMS (DCI- CH_4): m/z calcd for $\text{C}_{27}\text{H}_{41}\text{N}_3\text{P}$: 438.3038 [$\text{M}+\text{H}$] $^+$; found: 438.3034.

Phosphonium salt 5b: A solution of CBr_4 (6.98 g, 21.0 mmol) in dichloromethane (20 mL) was added dropwise at -80°C to a solution of cyclic phosphazene **4b** (9.20 g, 21.0 mmol) in dichloromethane (20 mL). After stirring for 1 h at -80°C , the solution was warmed up to room temperature. All the volatiles were removed under vacuum and the crude was washed with diethyl ether (3 x 10 mL). Phosphonium salt **5b** was obtained as a brownish powder (8.2 g, 75 % yield). M.p. = $136\text{--}137^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, CDCl_3): $\delta = 66.3$; ^1H NMR (300.1 MHz, 298 K, CDCl_3): $\delta = 1.36$ (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 1.38 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 4.01 (sept d, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HP}} = 12.9$ Hz, 4H, NCHCH_3), 7.29–7.32 (m, 3H, CH_{Ar}), 7.38–7.42 (m, 3H, CH_{Ar}), 7.50–7.54 (m, 2H, CH_{Ar}), 7.68–7.70 (m, 2H, CH_{Ar}), 8.83 (d, $^2J_{\text{HP}} = 30.6$ Hz, PCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, CDCl_3): $\delta = 22.5$ (s, NCHCH_3), 22.8 (s, NCHCH_3), 48.5 (d, $^2J_{\text{CP}} = 3.9$ Hz, NCHCH_3), 128.6 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 130.8 (s, CH_{Ar}), 132.4 (d, $^3J_{\text{CP}} = 23.6$ Hz, C_{ipso}), 133.3 (d, $^3J_{\text{CP}} = 28.9$ Hz, C_{ipso}), 134.1 (s, CH_{Ar}), 134.7 (d, $^1J_{\text{CP}} = 101.8$ Hz, PCH), 156.8 (d, $^2J_{\text{CP}} = 34.3$ Hz, $\text{NC}=\text{C}$), 183.5 (d, $^2J_{\text{CP}} = 7.1$ Hz, $\text{N}=\text{C}$); HRMS (DCI- CH_4): m/z calcd for $\text{C}_{27}\text{H}_{39}\text{N}_3\text{P}$: 436.2882 [M] $^+$; found: 436.2897.

Phosphonium salt 5'b: Trimethylsilyltriflate (5.1 mL, 28.0 mmol) was added drop by drop at -80°C to a solution of phosphonium salt **5b** (13.11 g, 25.4 mmol) in dichloromethane (60 mL). After 30 min, the solution was warmed up to room temperature and the volatiles removed under vacuum. The crude was washed with diethyl ether (3 x 20 mL). Then phosphonium salt **5'b** was obtained as colorless crystals from a saturated CH_2Cl_2 -THF solution (7.9 g, 53 % yield). M.p. = $137\text{--}138^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, CDCl_3): $\delta = 66.1$; ^{29}Si NMR (59.0 MHz, 298 K, CDCl_3): $\delta = 28.1$; ^{19}F NMR (282.4 MHz, 298 K, CDCl_3): $\delta = -77.4$; ^1H NMR (300.1 MHz, 298 K, CDCl_3): $\delta = 1.29$ (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 1.34 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 3.92 (sept, $^3J_{\text{HH}} = 6.6$ Hz, 4H, NCHCH_3), 7.20 (m, 2H, CH_{Ar}), 7.37 (m, 1H, CH_{Ar}), 7.39 (m, 2H, CH_{Ar}), 7.43 (m, 2H, CH_{Ar}), 7.50 (m, 1H, CH_{Ar}), 7.61 (m, 2H, CH_{Ar}), 7.93 (d, $^2J_{\text{HP}} = 30.9$ Hz, PCH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, CDCl_3): $\delta = 22.2$ (d, $^3J_{\text{CP}} = 1.4$ Hz, NCHCH_3), 22.3 (d, $^3J_{\text{CP}} = 1.2$ Hz, NCHCH_3), 48.3 (d, $^2J_{\text{CP}} = 4.8$ Hz, NCHCH_3), 120.9 (q, $^1J_{\text{CF}} = 318.8$ Hz, CF_3), 128.3 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 130.3 (s, CH_{Ar}), 130.9 (s, CH_{Ar}), 132.3 (d, $^3J_{\text{CP}} = 24.1$ Hz, C_{ipso}), 132.9 (d, $^3J_{\text{CP}} = 28.7$ Hz, C_{ipso}), 133.2 (d, $^1J_{\text{CP}} = 102.7$ Hz, PCH), 134.2 (s, CH_{Ar}), 157.2 (d, $^2J_{\text{CP}} = 33.4$ Hz, $\text{NC}=\text{C}$), 183.2

(d, $^2J_{\text{CP}} = 7.4$ Hz, $\text{N}=\text{C}$); HRMS (DCI- CH_4): m/z calcd for $\text{C}_{27}\text{H}_{39}\text{N}_3\text{P}$: 436.2882 [M] $^+$; found: 436.2881.

Azavinylidene phosphorane 6b: Phosphonium salt **5'b** (100 mg, 0.17 mmol) and potassium hexamethyldisilazane (35 mg, 0.17 mmol) were dissolved in 0.6 mL of $[\text{D}_8]\text{THF}$ at -80°C . Cyclic azavinylidene phosphorane **6b** was obtained and characterized by multinuclear NMR spectroscopy at -80°C without further purification. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 193 K, $[\text{D}_8]\text{THF}$): $\delta = 95.8$; ^1H NMR (300.1 MHz, 193 K, $[\text{D}_8]\text{THF}$): $\delta = 1.42$ (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, NCHCH_3), 1.44 (d, $^3J_{\text{HH}} = 7.8$ Hz, 12H, NCHCH_3), 4.50 (m, 4H, NCHCH_3), 7.30 (m, 3H, CH_{Ar}), 7.45 (m, 2H, CH_{Ar}), 7.49 (m, 2H, CH_{Ar}), 7.61 (m, 3H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 193 K, $[\text{D}_8]\text{THF}$): $\delta = 23.2$ (s, NCHCH_3), 42.4 (s, NCHCH_3), 123.9 (s, CH_{Ar}), 125.0 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 135.5 (d, $^3J_{\text{CP}} = 40.4$ Hz, C_{ipso}), 142.1 (d, $^3J_{\text{CP}} = 56.7$ Hz, C_{ipso}), 156.6 (d, $^2J_{\text{CP}} = 9.2$ Hz, $\text{NC}=\text{C}$), 175.9 (d, $^2J_{\text{CP}} = 42.1$ Hz, $\text{N}=\text{C}$), 234.4 (d, $^1J_{\text{CP}} = 93.6$ Hz, $\text{P}=\text{C}$).

Azaphosphetane 7: Phosphonium salt **5'b** (60 mg, 0.10 mmol) and potassium hexamethyldisilazane (20 mg, 0.10 mmol) were dissolved in 0.6 mL of $[\text{D}_8]\text{THF}$ at -80°C . The solution was slowly warmed up to room temperature. Azaphosphetane **7** was obtained quantitatively (indicated by ^{31}P NMR) and analyzed without further purification (43.5 mg). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, C_6D_6): $\delta = 66.6$; ^1H NMR (300.1 MHz, 298 K, C_6D_6): $\delta = 0.88$ (d, $^3J_{\text{HH}} = 6.3$ Hz, 3H, NCHCH_3), 1.14 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, NCHCH_3), 1.26 (d, $^3J_{\text{HH}} = 6.3$ Hz, 6H, NCHCH_3), 1.28 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H, NCHCH_3), 1.33 (s, 3H, NCCCH_3), 1.44 (s, 3H, NCCCH_3), 3.18 (sept, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{PH}} = 7.8$ Hz, 1H, NCHCH_3), 3.37 (d, $^2J_{\text{HP}} = 12.0$ Hz, 1H, PCH), 3.63 (m, 2H, NCHCH_3), 6.81–6.87 (m, 2H, CH_{Ar}), 7.04–7.08 (m, 3H, CH_{Ar}), 7.09–7.11 (m, 2H, CH_{Ar}), 7.18–7.20 (m, 2H, CH_{Ar}), 7.91–7.94 (m, 1H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, C_6D_6): $\delta = 21.3$ (d, $^3J_{\text{CP}} = 5.6$ Hz, NCCCH_3), 22.4 (s large, NCHCH_3), 22.9 (s large, NCHCH_3), 23.4 (d, $^3J_{\text{CP}} = 6.6$ Hz, NCHCH_3), 24.1 (d, $^3J_{\text{CP}} = 6.1$ Hz, NCHCH_3), 32.4 (d, $^3J_{\text{CP}} = 10.3$ Hz, NCCCH_3), 44.7 (d, $^2J_{\text{CP}} = 3.8$ Hz, NCHCH_3), 47.4 (d, $^2J_{\text{CP}} = 4.9$ Hz, NCHCH_3), 61.9 (d, $^1J_{\text{CP}} = 54.7$ Hz, PCH), 66.7 (d, $^2J_{\text{CP}} = 6.7$ Hz, $\text{NC}(\text{CH}_3)_2$), 110.8 (d, $^2J_{\text{CP}} = 17.3$ Hz, $\text{N}=\text{C}=\text{C}$), 122.5 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 129.6 (s, CH_{Ar}), 141.3 (d, $^3J_{\text{CP}} = 15.6$ Hz, C_{ipso}), 142.4 (d, $^3J_{\text{CP}} = 30.1$ Hz, C_{ipso}), 162.7 (d, $^2J_{\text{CP}} = 17.2$ Hz, $\text{N}=\text{C}$).

Spiro phosphazene 8: Phosphonium salt **5'b** (60 mg, 0.10 mmol) and potassium hexamethyldisilazane (20 mg, 0.10 mmol) were dissolved in 0.7 mL of $[\text{D}_8]\text{THF}$ at -80°C . After 30 min, methylacrylate (18.9 μL , 0.21 mmol) was added and the solution was kept at -60°C for 48 h. Spiro derivative **8** was obtained quantitatively as indicated by ^{31}P NMR. This product is not stable at room temperature and was analyzed by multinuclear NMR at -40°C . $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, 233 K, $[\text{D}_8]\text{THF}$): $\delta = 75.7$; ^1H NMR (400.1 MHz, 233 K, $[\text{D}_8]\text{THF}$): $\delta = 1.32$ (m, 6H, NCHCH_3), 1.41 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, NCHCH_3), 1.42 (m, 1H, $\text{CH}_{2\text{cycle}}$), 1.48 (m, 6H, NCHCH_3), 1.89 (ddd, $^2J_{\text{HH}} = 4.0$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, $^3J_{\text{HP}} = 13.0$ Hz, 1H, $\text{CH}_{2\text{cycle}}$), 2.10 (ddd, $^3J_{\text{HH}} = 5.6$ Hz, $^3J_{\text{HH}} = 6.4$ Hz, $^3J_{\text{HP}} = 7.6$ Hz, 1H, $\text{CH}_{2\text{cycle}}$), 3.66 (m, 1H, NCHCH_3), 3.69 (s, 3H, OCH_3), 3.99 (m, 1H, NCHCH_3), 4.09 (m, 2H, NCHCH_3), 7.00–7.01 (m, 3H, CH_{Ar}), 7.01–7.02 (m, 2H, CH_{Ar}), 7.20–7.21 (m, 1H, CH_{Ar}), 7.26–7.28 (m, 2H, CH_{Ar}), 7.39–7.41 (m, 2H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.1 MHz, 233 K, $[\text{D}_8]\text{THF}$): $\delta = 21.3$ (s, NCHCH_3), 22.3 (d, $^2J_{\text{CP}} = 2.8$ Hz, $\text{CH}_{2\text{cycle}}$), 22.5 (s, NCHCH_3), 25.1 (d, $^3J_{\text{CP}} = 3.2$ Hz, NCHCH_3), 26.6 (d, $^2J_{\text{CP}} = 7.2$ Hz, $\text{CH}_{2\text{cycle}}$), 37.3 (d, $^1J_{\text{CP}} = 96.7$ Hz, $\text{P}=\text{C}$), 47.1 (s, NCHCH_3), 47.6 (s, NCHCH_3), 47.9 (s, NCHCH_3), 51.7 (s, OCH_3), 109.6 (d, $^2J_{\text{CP}} = 36.6$ Hz, $\text{NC}=\text{C}$), 125.8 (s, CH_{Ar}), 126.6 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 138.3 (d, $^3J_{\text{CP}} = 12.8$ Hz, C_{ipso}), 139.9 (d, $^3J_{\text{CP}} = 24.6$ Hz, C_{ipso}), 151.9 (d, $^2J_{\text{CP}} = 8.1$ Hz, $\text{N}=\text{C}$), 172.4 (d, $^3J_{\text{CP}} = 5.3$ Hz, $\text{C}=\text{O}$).

Spiro phosphonium salt 9: Phosphonium salt **5'b** (182 mg, 0.31 mmol) and potassium hexamethyldisilazane (61.7 mg, 0.31 mmol) were dissolved in 3.0 mL of THF at -80°C . After 30 min, methylacrylate (56 μL , 0.62 mmol) was added and the solution was kept at -60°C for 48 h. One equivalent of methyltriflate (35 μL , 0.31 mmol) was added -60°C then the solution was warmed up to room temperature. All volatiles were removed under vacuum, and the crude was washed with diethyl ether (3 x 2 mL). Spiro phosphonium salt **9** was obtained as

a white powder (95.6 mg, 45 % yield). M.p. = 142–144 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, CDCl_3): δ = 72.7; ^1H NMR (300.1 MHz, 298 K, CDCl_3): δ = 1.45 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, NCHCH_3), 1.48 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, NCHCH_3), 1.49 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, NCHCH_3), 1.50 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, NCHCH_3), 1.52 (m, 1H, $\text{CH}_{2\text{cycle}}$), 2.11 (ddd, $^2J_{\text{HH}} = 4.5$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HP}} = 16.5$ Hz, 1H, $\text{CH}_{2\text{cycle}}$), 2.49 (ddd, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HH}} = 9.0$ Hz, $^3J_{\text{HP}} = 16.5$ Hz, 1H, $\text{CH}_{2\text{cycle}}$), 2.75 (d, $^3J_{\text{HP}} = 10.5$ Hz, 3H, NCH_3), 3.79 (s, 3H, OCH_3), 3.95 (sept d, $^3J_{\text{HH}} = 6.6$ Hz, $^2J_{\text{HP}} = 13.2$ Hz, 2H, NCHCH_3), 4.03 (sept d, $^3J_{\text{HH}} = 7.2$ Hz, $^2J_{\text{HP}} = 14.4$ Hz, 2H, NCHCH_3), 6.80–6.89 (m, 2H, CH_{Ar}), 6.94–7.05 (m, 2H, CH_{Ar}), 7.19–7.21 (m, 3H, CH_{Ar}), 7.21–7.22 (m, 3H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, CDCl_3): δ = 22.1 (d, $^3J_{\text{CP}} = 0.8$ Hz, NCHCH_3), 23.7 (s, NCHCH_3), 23.8 (s, NCHCH_3), 23.9 (s, $\text{CH}_{2\text{cycle}}$), 25.2 (d, $^3J_{\text{CP}} = 2.2$ Hz, NCHCH_3), 29.4 (d, $^3J_{\text{CP}} = 5.7$ Hz, $\text{CH}_{2\text{cycle}}$), 30.6 (d, $^1J_{\text{CP}} = 134.4$ Hz, PC), 34.9 (d, $^2J_{\text{CP}} = 1.0$ Hz, NCH_3), 49.9 (d, $^2J_{\text{CP}} = 4.8$ Hz, NCHCH_3), 50.0 (d, $^2J_{\text{CP}} = 4.9$ Hz, NCHCH_3), 53.1 (s, OCH_3), 116.5 (d, $^2J_{\text{CP}} = 18.6$ Hz, $\text{NC}=\text{C}$), 126.4 (s, CH_{Ar}), 126.6 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 129.6 (d, $^3J_{\text{CP}} = 8.1$ Hz, C_{ipso}), 130.2 (d, $^3J_{\text{CP}} = 9.5$ Hz, C_{ipso}), 131.2 (s, CH_{Ar}), 170.3 (d, $^2J_{\text{CP}} = 5.6$ Hz, N-C), 174.8 (s, $\text{C}=\text{O}$); HRMS (DCI-CH_4) m/z calcd for $\text{C}_{32}\text{H}_{47}\text{N}_3\text{O}_2\text{P}$ 536.3406 [M^+]; found: 536.3412.

Rhodium cyclooctadiene complex 10: Phosphonium salt **5'b** (100 mg, 0.17 mmol) and potassium hexamethyldisilazane (35 mg, 0.18 mmol) were dissolved in 2 mL of THF at -80 °C. After 30 min, a solution of $[\text{RhCl}(\text{COD})]_2$ (42 mg, 0.085 mmol) in THF (1 mL) was added and stirred for 15 h at -80 °C. Then the solution was warmed up to room temperature and the volatiles removed under vacuum. The crude was washed with diethyl ether (2 x 2 mL) and complex **10** was extracted with dichloromethane. Red crystal of **10** were grown from a dichloromethane-diethyl ether solution at -30 °C (82 mg, 71 % yield). M.p. = 159–161 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 80.9 (d, $^2J_{\text{PRh}} = 6.2$ Hz); ^1H NMR (300.1 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 1.46 (d, $^3J_{\text{HH}} = 4.2$ Hz, 12H, NCHCH_3), 1.50 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, NCHCH_3), 1.73 (s, 4H, CH_2), 2.18 (s, 4H, CH_2), 3.34 (s, 2H, CH), 4.11 (s, 4H, NCHCH_3), 4.79 (s, 2H, CH), 7.23–7.46 (m, 2H, CH_{Ar}), 7.27–7.28 (m, 2H, CH_{Ar}), 7.29–7.30 (m, 1H, CH_{Ar}), 7.39–7.42 (m, 1H, CH_{Ar}), 7.43–7.46 (m, 2H, CH_{Ar}), 7.72–7.75 (m, 2H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 23.8 (s, NCHCH_3), 23.9 (s, NCHCH_3), 28.6 (s, CH_2), 32.6 (s, CH_2), 48.9 (d, $^2J_{\text{CP}} = 4.9$ Hz, NCHCH_3), 66.7 (s, CH), 94.7 (s, CH), 126.7 (s, CH_{Ar}), 126.9 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 129.7 (s, CH_{Ar}), 130.4 (s, CH_{Ar}), 131.1 (s, CH_{Ar}), 136.4 (d, $^3J_{\text{CP}} = 32.3$ Hz, C_{ipso}), 141.4 (d, $^3J_{\text{CP}} = 37.9$ Hz, C_{ipso}), 156.3 (d, $^2J_{\text{CP}} = 30.9$ Hz, N-C), 180.0 (dd, $^2J_{\text{CP}} = 20.9$ Hz, $^2J_{\text{CRh}} = 3.4$ Hz, $\text{NC}=\text{C}$), 195.8 (dd, $^1J_{\text{CP}} = 41.2$ Hz, $^1J_{\text{CRh}} = 7.6$ Hz, PC); HRMS (DCI-CH_4) m/z calcd for $\text{C}_{35}\text{H}_{50}\text{N}_3\text{PClRh}$: 681.2486 [$\text{M}+\text{H}^+$]; found: 681.2469.

Rhodium carbonyl complex 11: Carbon monoxide is bubbled into a solution of rhodium cyclooctadiene complex **10** (50 mg, 0.07 mmol) in dichloromethane (2 mL) at room temperature. The solution turns from red to yellow, then all the volatiles were removed under vacuum. **11** is obtained as a yellow powder (46.1 mg, 90 % yield); IR (THF): ν = 2066, 1990 cm^{-1} (CO); m.p. = 130–132 °C; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 84.6 (d, $^2J_{\text{PRh}} = 6.7$ Hz); ^1H NMR (300.1 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 1.27 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 1.38 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, NCHCH_3), 4.22 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, NCHCH_3), 7.14–7.19 (m, 3H, CH_{Ar}), 7.21–7.24 (m, 2H, CH_{Ar}), 7.29–7.32 (m, 2H, CH_{Ar}), 7.38–7.40 (m, 3H, CH_{Ar}); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, 298 K, $[\text{D}_8]\text{THF}$): δ = 23.6 (d, $^3J_{\text{CP}} = 1.7$ Hz, NCHCH_3), 23.8 (d, $^3J_{\text{CP}} = 2.9$ Hz, NCHCH_3), 48.8 (d, $^2J_{\text{CP}} = 4.9$ Hz, NCHCH_3), 127.2 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 130.4 (s, CH_{Ar}), 131.9 (s, CH_{Ar}), 135.2 (d, $^3J_{\text{CP}} = 31.4$ Hz, C_{ipso}), 140.8 (d, $^3J_{\text{CP}} = 36.4$ Hz, C_{ipso}), 159.5 (d, $^2J_{\text{CP}} = 29.7$ Hz, N-C), 177.9 (dd, $^1J_{\text{CP}} = 35.8$ Hz, $^1J_{\text{CRh}} = 23.6$ Hz, PC), 181.4 (dd, $^2J_{\text{CP}} = 18.5$ Hz, $^2J_{\text{CRh}} = 2.9$ Hz, $\text{N-C}=\text{C}$), 183.5 (d, $^1J_{\text{CRh}} = 74.2$ Hz, CO), 185.4 (dd, $^1J_{\text{CRh}} = 52.5$ Hz, $^3J_{\text{CP}} = 10.4$ Hz, CO).

Computational details

All the geometries have been fully optimized at the B3LYP^[26] density functional level of calculation. The 6-31G(d) basis set has been used for main group elements.^[27] For Rh we have used the LANL2DZ basis set in which the inner electrons are represented by an effective core potential.^[28] Harmonic vibrational

frequencies have been computed for all structures to verify that they correspond to energy minima (all frequencies are real). The stretching CO frequencies of complexes with $\text{Rh}(\text{CO})_2\text{Cl}$ have been scaled by 0.9614.^[29] The electronic structure of all systems has been analyzed using the NBO method.^[30] Wiberg bond indexes^[31] were computed within the NBO method. The structure of the triplet of **6b** has been optimized using an unrestricted spin formalism. The reported S/T energy gap includes the zero-point vibrational energy correction. Electrophilicities (ω) and maximum electronic charges (ΔN_{max}) were calculated according to the definitions proposed by Parr, Yang et al.:

$$\omega = \frac{\mu^2}{2\eta}$$

$$\Delta N_{\text{max}} = -\frac{\mu}{\eta}$$

where the corresponding chemical potentials (μ) and the hardnesses (η) were computed within the ground-state parabola model^[32] according to the following approximate expressions related to the orbital energies of the Kohn-Sham frontier orbitals:

$$\mu \approx (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) / 2$$

$$\eta \approx \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$$

All calculations have been done using the Gaussian-09 suite of programs.^[33]

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

FULL PAPER

A novel family of cyclic push-pull carbenes, namely azavinylidene phosphoranes were synthesized by a formal [3+2] cycloaddition, followed by oxidation / deprotonation steps. Carbenes exhibit pronounced ambiphilic character (C-H insertion, cycloaddition reactions), confirmed by DFT calculations (S/T energy gap ~ 24 kcal.mol⁻¹). In addition, they present excellent coordination abilities toward transition metals due to the cyclic structure.

■ Carbene Chemistry

F. Lavigne, A. El Kazzi, Y. Escudié, E. Maerten, T. Kato, N. Saffon-Merceron, V. Branchadell, F. P. Cossío and A. Baceiredo**

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Azavinylidenephosphoranes: a new class of cyclic push-pull carbenes