

Stable P-Heterocyclic Carbenes: Scope and Limitations

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Abstract: The conjugate acids (PHCH⁺s) of P-heterocyclic carbenes (PHCs) are prepared by formal [3+2] cycloaddition of a 1,3-diphosphaallyl or 1,3-phosphinophosphenium cation with various nitriles. The effect of the phosphorus substituent on the fate of the cyclization and on that of the counteranion and base in the subsequent deprotonation reaction are reported. Two PHCs that are indefinitely stable in the solid state are described. In solution,

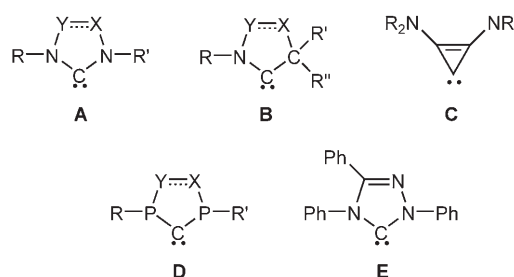
one of them, made from acetonitrile, undergoes a facile [3+2] cycloreversion, whereas the other, based on dimethyl cyanamide, is stable, presumably owing to its zwitterionic structure, which involves a tricoordinate pentavalent phosphorus atom. The reactivity of

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PHCs is strongly driven by the high electrophilicity of the phosphorus centers, as demonstrated by their reactivity with water and benzaldehyde. Although both PHCs reported in this paper are direct analogues of the least-basic NHCs, their basicity is comparable to those of the more strongly basic NHCs (as determined by comparison of the carbonyl stretching frequencies of their corresponding *cis*-[RhCl(CO)₂(L)] complexes).

Introduction

The ability to perform catalytic reactions more efficiently is at the forefront of many research programs in academia and industry. In transition-metal-based catalysis, the choice of the metal is obviously limited, but the nature of the ligands can, in principle, be modified at will. Traditionally, many homogeneous catalytic reactions have relied on the use of phosphines as ligands; their popularity is attributed to the ease with which the electronic and steric environments about the phosphorus atom can be tuned. In recent years, stable carbenes^[1] have become an attractive alternative to traditional phosphine-based ligands. Among the stable carbenes known thus far, the N-heterocyclic carbenes (NHCs) **A**^[2] have been by far the most frequently used (Scheme 1).



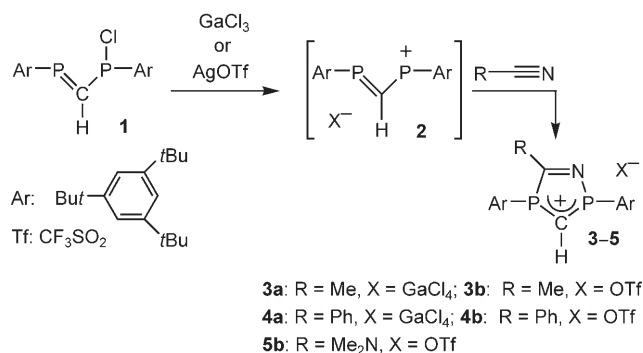
Scheme 1. Schematic representation of NHCs **A**, CAACs **B**, cyclopropenyldiene **C**, PHCs **D**, and the Enders carbene **E**.

Indeed, it was found that free acyclic carbenes are not only more fragile than NHCs, but the ensuing complexes are also less robust.^[3] It was suggested^[4] that the poor coordination behavior of acyclic carbenes may be due to the larger carbene bond angle, typically 116–124° compared to 101–106° for NHCs. Accordingly, we initiated a research program limited to stable cyclic carbenes. We have already shown that cyclic (alkyl)(amino)carbenes (CAACs) **B** are very stable and allow for the preparation of highly robust and active palladium catalysts for the α -arylation of carbonyl derivatives.^[5] More recently, we also showed that even carbocyclic carbenes, namely cyclopropenyldienes **C**, can be isolated,^[6] and the catalytic properties of the ensuing complexes are currently under investigation.

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NHCs **A**, CAACs **B**, and to a lesser extent cyclopropenylidenes **C** are stabilized by π -donation from the lone pair at the planar nitrogen atom(s) to the vacant orbital of the carbene center. Interestingly, it was predicted that the π -donor capabilities of heavier elements, especially phosphorus, can be the same as or greater than those of their second-row cousins, providing that a planar configuration can be achieved.^[7] As there are several methods available for inducing planarity at the phosphorus atom,^[8] among them being the inclusion of the heteroatoms in a ring system accompanied by the presence of bulky substituents, we decided to target P-heterocyclic carbenes (PHCs) **D** in which the two nitrogen atoms of NHCs **A** are replaced by phosphorus atoms.^[9–14]



Scheme 2. Synthesis of PHCH⁺s **3–5**.

Table 1. Selected spectroscopic data and geometric parameters.

	3	4	5	D1	D2	22	23	24 ^[14]
³¹ P NMR:								
δ [ppm]	104, 85	106, 80	113, 12	85, 73	14, 65	101, 93	29, 91	
² J _{PP} [Hz]	266	240	284	135	232	187	246	
¹³ C NMR:								
δ [ppm]	119	119	115	184	187	176	182	
¹ J _{PC} [Hz]	51, 44	62, 57	65, 7	147	153, 127	8, 2	12, 3	
Σ angles P1 [°]	354		354	353			355	
Σ angles P2 [°]	348		336	348			339	
P1–C1 [Å]	1.693		1.646	1.673			1.668	
P2–C1 [Å]	1.720		1.731	1.710			1.756	
$\tilde{\nu}_{CO}$ [cm ^{–1}]						1985, 2059	1981, 2062	2009, 2089

Results and Discussion

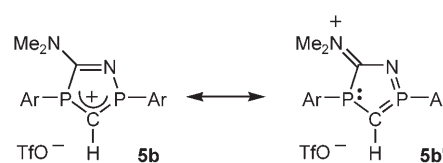
Synthesis of the Conjugate Acid of PHCs

The classical precursors for NHCs are the corresponding conjugate acids (NHCH⁺), which are readily available through well-established synthetic routes. However, these methods cannot be extended to the heavier congeners of NHCs such as PHCH⁺.^[15,16] Thus, we had to design an original synthetic approach: a formal [3+2] cycloaddition of the transient diphosphaallylic cation **2**, which bears bulky 2,4,6-tris(*tert*-butyl)phenyl substituents, with a dipolarophile (Scheme 2). Addition (at –78 °C) of gallium trichloride to a solution of phosphorane **1**^[17] in dichloromethane in the presence of a large excess of acetonitrile (30–45 equiv) afforded cleanly the desired salt **3a**, which was isolated as a white crystalline solid in 67% yield. Similarly, silver trifluoromethane sulfonate can also be used to abstract the chloride from **1**, and the corresponding salt **3b** was isolated in slightly better yield (80%).

With a synthetic route in hand, we investigated the possibility of varying 1) the substituents R at the imine carbon atom of the ring, 2) the nature of the ring backbone, and 3) the substituents at the phosphorus atom.

With nitriles, the formal [3+2] cycloaddition approach appears to be very general. Indeed, with benzonitrile and, more importantly, dimethyl cyanamide (see below), clean reactions occurred, and PHCH⁺s **4a**, **4b**, and **5b** were isolated in 76, 85, and 50% yields, respectively (Scheme 2). Not surprisingly, the NMR spectroscopic data for the C-phenyl derivatives **4** are very similar to those observed for the C-methyl compounds **3** (Table 1). In contrast, whereas the ³¹P NMR spectra of derivatives **3** and **4** show similar AX systems at 104 and 85 ppm (*J*_{PP} = 266 Hz) and 106 and 80 ppm (*J*_{PP} = 240 Hz), respectively, the C-amino derivative **5b** gives signals at 113 and 12 ppm (*J*_{PP} = 284 Hz). The high-field signal for **5b** suggests that the lone pair of one of the

phosphorus centers does not interact significantly with the electron-deficient carbon center. Moreover, the ¹H NMR spectrum reveals two methyl signals for the N(CH₃)₂ fragment, thus implying restricted rotation about the N–C bond. These results as a whole suggest an important contribution of a resonance structure featuring tricoordinate pentavalent and tricoordinate trivalent phosphorus centers, as shown by **5b'** (Scheme 3). A single-crystal X-ray diffraction study con-



Scheme 3. Resonance structures for PHCH⁺ **5b**.

firmed this hypothesis (Figure 1). The trigonal-planar configuration about N2 (sum of angles = 360°) and an N2–C2 bond length of 1.314(5) Å are both indicative of an iminium-like exocyclic nitrogen atom. Atom P1 is in a nearly planar environment (sum of angles = 354°), and P2 is significantly pyramidalized (sum of angles = 336°); these angles have to be compared with those observed for **3b** (354 and 348°, respectively; Table 1). Finally, the C1–P1 bond length of 1.646 Å is significantly lower than that of C1–P2 (1.731 Å) and falls within the typical range for a P–C

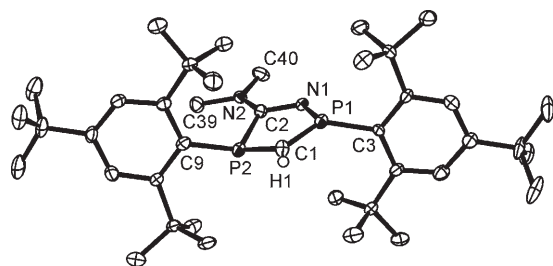
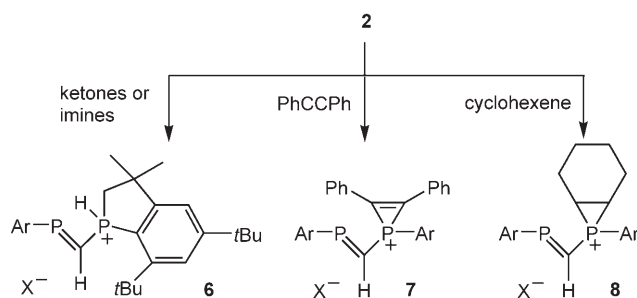


Figure 1. ORTEP view of the cationic part of $\text{PHCH}^+ \mathbf{5b}$ (50% thermal ellipsoids shown). Hydrogen atoms (except for H1) are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N1 1.636(3), P1–C1 1.646(4), P2–C1 1.731(4), P2–C2 1.832(5), N1–C2 1.347(5), N2–C2 1.314(5); N1–P1–C1 108.28(19), N1–P1–C3 118.17(19), C1–P1–C3 127.3(2), C1–P2–C9 119.8(2), C1–P2–C2 96.9(2), C9–P2–C2 119.4(2), C2–N2–C39 121.8(3), C2–N2–C40 120.9(3), C39–N2–C40 117.3(3), P1–C1–P2 107.1(2).

double bond; similarly, the short P1–N1 bond (1.636 Å) suggests some degree of P–N multiple-bond character.

To prepare PHCs with different backbones, we attempted to trap the transient diphosphaallylic cation **2** with other dipolarophiles (Scheme 4). However, the intermediate **2** ap-



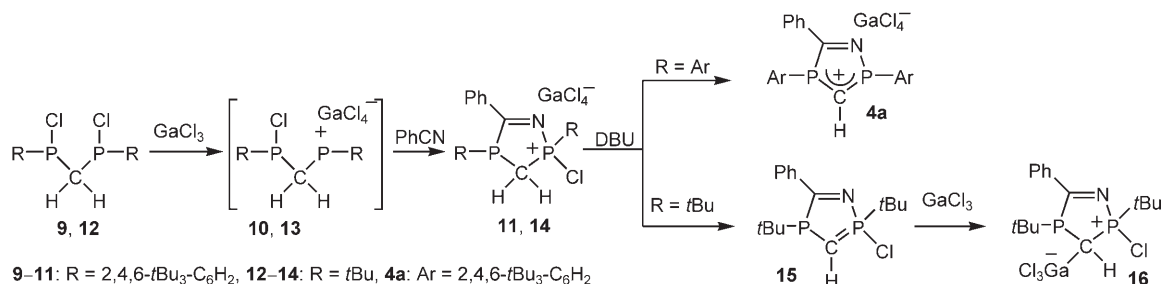
Scheme 4. Trapping reactions of diphosphaallyl cation **2**.

peared inert towards both ketones and imines; it preferentially undergoes an intramolecular insertion of the phosphonium center into a C–H bond of a *tert*-butyl substituent, quantitatively forming the cyclic phosphonium salt **6**.^[17] With diphenyl ethyne and cyclohexene, clean reactions occurred, but instead of the desired five-membered heterocyclic adducts, phosphirenium **7** and phosphiranium **8** were formed.^[18] These results clearly suggest that five-membered heterocycles **3–5** do not result from concerted [3+2] cyclo-

additions, but from the nucleophilic attack of the nitrogen end of the nitrile on a positively charged phosphorus center, followed by 1,5-ring closure.

As the double bond of the transient diphosphaallylic cation **2** was not involved in the first step of the cyclization, we developed a second route to PHCH^+ s starting from the readily available 1,3-dichloro-1,3-diphosphapropanes **9** (Scheme 5).^[17b,19] Addition of GaCl_3 to **9** led to the transient phosphonium salt **10**, which then reacted with excess benzonitrile (10 equiv) to afford the five-membered heterocycle **11**. Dehydrohalogenation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave rise to the desired gallium salt **4a** in 83% yield. This method seemed particularly promising for easy variation of the substituents at the phosphorus center. Indeed, diphosphaallyl chlorides of type **1** are only stable when both phosphorus centers bear sterically bulky aryl substituents. In contrast, 1,3-dichloro-1,3-diphosphapropane derivatives such as **9** are readily available with different substituents on phosphorus.^[20]

Reaction of the *tert*-butyl derivative **12** with GaCl_3 in the presence of an excess of benzonitrile in cold CH_2Cl_2 gave the desired phosphonium salt **14**, analogous to **11**, in moderate yield. ^{31}P and ^1H NMR spectra revealed signals from inequivalent phosphorus centers at 103 and 106 ppm and two magnetically distinct *t*Bu groups. However, treatment of cyclic phosphonium salt **14** with DBU did not induce the expected dehydrohalogenation reaction; rather, it resulted in the formal loss of " HGaCl_4 " to give ylide **15**, as shown by a ^1H NMR signal at 2.26 ppm (dd, $J_{\text{PH}} = 25, 31$ Hz). Clearly, the *tert*-butyl groups are not bulky enough to protect the phosphorus centers adequately or force their planarization, a requirement of $1\sigma^4, 3\sigma^4$ -diphosphaallylic cation stability.^[15] An attempt to abstract chloride from **15** with GaCl_3 resulted in the formation of a highly unstable material with ^{31}P NMR signals at 81 and 154 ppm. However, a freshly prepared solution of pentane cooled to -10°C gave single crystals suitable for X-ray analysis, which allowed the structural characterization of **16**, the gallium trichloride adduct of **15** (Figure 2). Overall, the structure reveals two *t*Bu groups on the same side of the ring, with a GaCl_3 fragment pointing toward the other side. Interestingly, the tricoordinate phosphorus atom P2 is highly pyramidalized (sum of angles = 301°), suggesting that *t*Bu substituents would not fulfill the requirements for the formation of a stable PHC.



Scheme 5. Alternative route to PHCH^+ s: influence of the substituents.

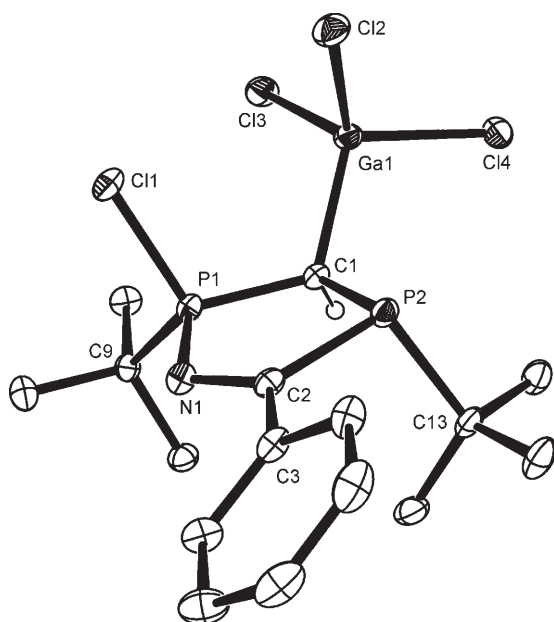
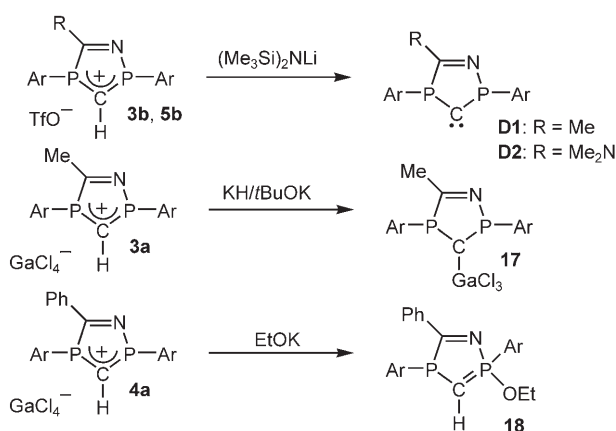


Figure 2. ORTEP view of **16** (50% thermal ellipsoids shown). Hydrogen atoms (except for H1) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–C1 2.019(2), C1–P1 1.778(2), C1–P2 1.872(2), P1–N1 1.6588(18), N1–C2 1.308(3); P1–C1–P2 105.33(11), P1–C1–Ga1 117.82(11), P2–C1–Ga1 109.00(10), N1–P1–C1 106.14(9), N1–P1–C9 110.14(10), C1–P1–C9 119.42(10), N1–P1–Cl1 104.21(7), C1–P1–Cl1 110.35(8), C9–P1–Cl1 105.61(7), C2–N1–P1 113.31(15), N1–C2–C3 118.5(2), N1–C2–P2 120.20(16), C3–C2–P2 121.28(16), C2–P2–C1 93.80(9), C2–P2–C13 102.19(10), C1–P2–C13 104.70(10).

Deprotonation of the Conjugate Acids of PHCs

Deprotonation of PHCH⁺ triflate **3b** in THF at –78°C, with lithium bis(trimethylsilyl)amide as base, cleanly led to PHC **D1** (Scheme 6). This carbene was isolated after recrystallization from a concentrated solution of THF/toluene at –30°C as light-yellow crystals (72% yield). Similarly, deprotonation of **5b** can be performed with either lithium or potassium bis(trimethylsilyl)amide in THF at –78°C. Upon workup, carbene **D2** was isolated in 66% yield as a yellow powder. The ¹³C NMR signal for carbene for **D2** appears at



Scheme 6. Reactions of PHCH⁺s with various bases.

187 ppm as a doublet of doublets ($J_{\text{PC}}=127, 153$ Hz), in a similar region to that of **D1** (184 ppm, tripletlike, $J_{\text{PC}}=147$ Hz). However, the distinctly unsymmetrical P^V/P^{III} nature of carbene **D2** is reflected once again in the ³¹P NMR spectrum with signals at 14 and 65 ppm ($J_{\text{PP}}=232$ Hz), whereas for **D1** both signals were found at relatively low field (73 and 85 ppm, $J_{\text{PP}}=135$ Hz). Several X-ray diffraction datasets of **D2** were collected, but unfortunately all were plagued with twinning and/or disorder problems, thus precluding a reliable structure solution.

During our investigations, we found that the nature of the counteranion/base combination has a crucial influence on the fate of the deprotonation reaction. When **3a** (GaCl₄[–] as counteranion) was deprotonated with KH/*t*BuOK, the free carbene was not formed; instead, its GaCl₃ adduct **17** was obtained in 83% yield (Scheme 6). The ³¹P NMR spectrum of **17** revealed two sets of doublets at 94 and 114 ppm ($J_{\text{PP}}=225$ Hz) that were shifted to lower field compared to the signals of the free carbene (73 and 85 ppm). The single-crystal X-ray structure (Figure 3) reveals GaCl₃ coordinated to the

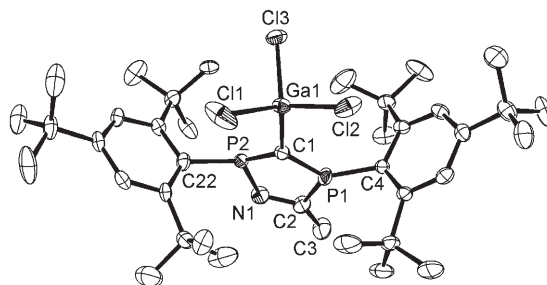


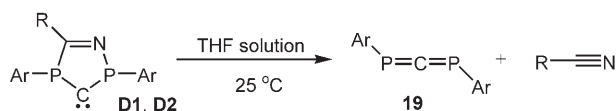
Figure 3. ORTEP view of gallium-carbene complex **17** (50% thermal ellipsoids shown). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1–C1 1.994(4), C1–P1 1.690(4), C1–P2 1.746(5), C2–N1 1.366(12), C2–C3 1.501(7), C2–P1 1.718(5), N1–P2 1.666(11); P1–C1–P2 100.7(2), P1–C1–Ga1 129.8(3), P2–C1–Ga1 126.4(2), N1–C2–C3 114.4(6), N1–C2–P1 114.1(5), C3–C2–P1 130.1(4), C2–N1–P2 110.2(7), C1–P1–C2 105.2(2), C1–P1–C4 123.3(2), C2–P1–C4 131.3(2), N1–P2–C1 108.0(4), N1–P2–C22 119.6(12), C1–P2–C22 121.6(11).

carbene center, with a gallium–carbon bond length of 1.99 Å, which is significantly shorter than those of analogous NHC complexes (2.079 Å),^[21a,b] but longer than that observed for a phosphinocarbene–GaCl₃ complex (1.978 Å).^[21c] Interestingly, one of the phosphorus atoms is in a perfectly planar environment (P1, sum of angles = 360°), whereas the second is slightly pyramidalized (P2, sum of angles = 349°), making the molecule chiral in the solid state. As the P1–C1 bond length (1.69 Å) is significantly shorter than that of P2–C1 (1.75 Å), it is clear that the P1 atom interacts more strongly than P2 with the electron-deficient carbene center. The value of the P1–C1–P2 bond angle for **17** (100.7°) is closer to that of the free carbene **D1** (98.2°) than that of its cationic precursor **3** (106.2°). Here again, a similar trend to the case of NHCs was observed.^[1,2]

When potassium ethoxide and **4a** (GaCl_4^- as counteranion) were used as base and cationic precursor, respectively, the free carbene was again not formed. Elimination of GaCl_3 and KCl occurred, and ylide **18** was obtained in 70% yield (Scheme 6). The presence of the ylidic CH fragment was apparent from ^1H and ^{13}C NMR signals at 2.40 (dd, $J_{\text{PH}}=15, 35$ Hz) and 27.7 ppm (dd, $J_{\text{PC}}=7, 111$ Hz), respectively. This highlights a major discrepancy between the chemistry of PHCH^+ s and NHCH^+ s, their nitrogen analogues. Because phosphorus can be hypervalent and is more electronegative than carbon, attack of ethoxide occurs at the phosphorus center. This behavior parallels the chemistry of methylenephosphonium^[22] and iminium salts. The former react with nucleophiles at phosphorus, whereas the latter react at carbon.

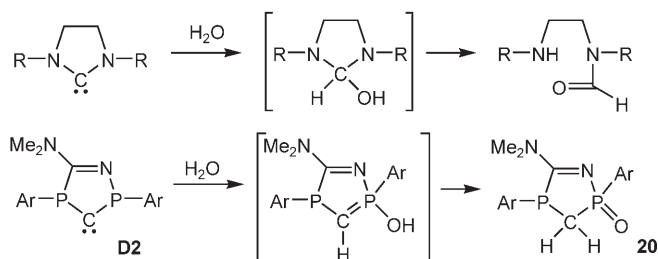
Stability, Reactivity, and Coordination Behavior of PHCs

Although in the solid state PHC **D1** is indefinitely stable at room temperature (m.p.: 123–127 °C), it readily undergoes a [3+2] retrocycloaddition in solution to afford the previously described 1,3-diphosphaallene **19**^[23] and acetonitrile (Scheme 7). This reaction clearly shows first-order kinetics



Scheme 7. Fragmentation of PHCs **D1** and **D2** in solution.

(monitored by ^{31}P NMR spectroscopy), and the half-life of **D1** is about 5 h at 16 °C in THF. This behavior is very surprising as the nitrogen analogue, namely the Enders carbene **E** (Scheme 1),^[24] seems to be very stable in solution. Importantly, there is no evidence of retrocycloaddition of PHC **D2** after 24 h in THF at 25 °C. This is presumably owing to the zwitterionic resonance form analogous to **5b'** (with a tri-coordinate pentavalent P center), which significantly stabilizes the system thermodynamically. Carbene **D2** is, however, very sensitive to moisture, and slowly gives rise to the phosphine oxide **20** (Scheme 8) when exposed to air. According to the literature,^[25] NHCs also react with water, but give the corresponding amine/formamide. In both cases, the first step is presumably the protonation of the carbene center. For



Scheme 8. Comparative reactivity of PHCs versus NHCs with water.

NHCs there is a nucleophilic addition of OH^- at carbon, whereas for PHCs, attack occurs at the electrophilic phosphorus atom. Despite the bulkiness of the aryl groups, ^{31}P NMR spectroscopy revealed the presence of two isomers in solution (−8.1 and 56.8 ppm; −20.3 and 49.7 ppm) with a ratio that is solvent-dependent; a 1:1 mixture is formed in C_6D_6 , whereas in CDCl_3 the ratio changes to 3:1. The solid-state structure of the *cis* isomer was determined by a single-crystal X-ray diffraction study. The phosphine oxide fragment has a pseudotetrahedral geometry, and the phosphine is highly pyramidalized (sum of angles = 318°, Figure 4). These results demonstrate that the very bulky 2,4,6-*tert*-butylphenyl substituent does not force the phosphorus atom to be planar, but considerably reduces the inversion barrier. We also note that the aryl groups become distorted to accommodate the steric demands.

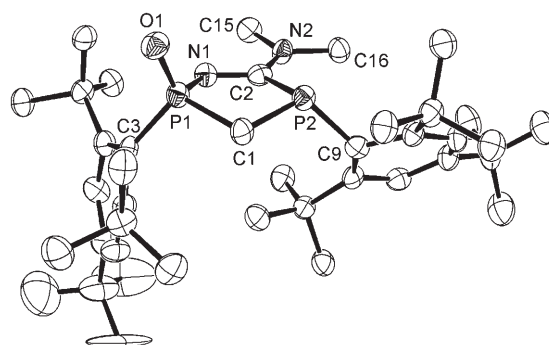
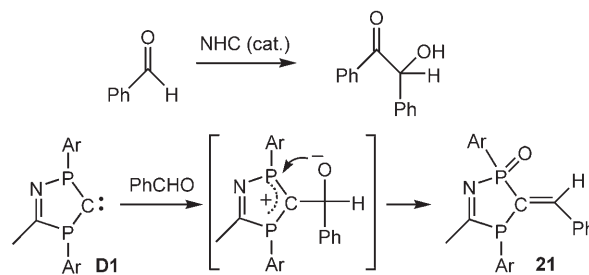


Figure 4. ORTEP view of **20** (50% thermal ellipsoids shown). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–O1 1.485(4), P1–N1 1.661(4), P1–C1 1.842(5), P2–C1 1.834(5), P2–C2 1.851(5), N1–C2 1.316(6), N2–C2 1.336(6); P2–C1–P1 105.5(2), C1–P2–C9 116.2(2), C1–P2–C2 93.6(2), C9–P2–C2 108.3(2), C2–N2–C16 124.1(4), C2–N2–C15 120.1(4), C16–N2–C15 115.8(4), N1–C2–N2 120.6(4), N1–C2–P2 117.6(4), N2–C2–P2 120.8(4), C2–N1–P1 116.8(3).

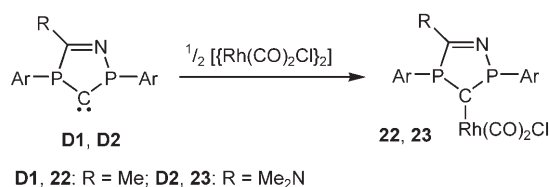
It is known that NHCs such as the Enders carbene **E** (Scheme 1) are catalysts for benzoin condensation.^[26] In marked contrast, reaction of PHC **D1** with benzaldehyde gave diphosphafulvene **21** (Scheme 9). Its ^{31}P NMR chemical shifts of 0 and 40 ppm are assigned to the P^{III} and P^{V} atoms, respectively. Also characteristic is the ethylenic hydrogen atom, whose signal appears at 8.50 ppm as a doublet of dou-



Scheme 9. Comparative reactivity of PHCs versus NHCs with benzaldehyde.

blets ($^3J_{\text{PH}} = 13, 20 \text{ Hz}$) due to coupling with two magnetically distinct phosphorus centers. This type of reactivity was observed with phosphinosilyl carbenes,^[27] although as the minor pathway;^[28a] the major product is the epoxides that result from a [2+1] cycloaddition process.^[28] In relation to NHCs, this difference in reactivity can be attributed to the propensity of the oxophilic phosphorus center to be oxidised to P^{V} , whereas in the case of NHCs, this possibility is clearly suppressed, allowing isomerization to the enolate and addition of a second equivalent of benzaldehyde.

To compare the ligand behavior of PHCs **D1** and **D2** with analogous NHCs, the rhodium carbonyl complexes **22** and **23** were prepared by addition of half an equivalent of $[\{\text{RhCl}(\text{CO})_2\}_2]$ to freshly prepared solutions of PHCs **D1** and **D2**, respectively, in THF (**22**: 69% yield, m.p.: 175–178 °C; **23**: 61% yield, m.p.: 123–126 °C) (Scheme 10). The



Scheme 10. Synthesis of $[\text{RhCl}(\text{CO})_2(\text{PHC})]$ complexes **22** and **23**.

^{13}C NMR chemical shifts for the carbene and CO carbon nuclei of **22** and **23** are comparable (C_{carb} : 175.9 (**22**), 182.1 ppm (**23**); CO: 183.9 and 185.9 (**22**), 183.7 and 185.5 ppm (**23**)), but here too the ^{31}P NMR spectra of the two complexes are quite different: 101 and 93 ppm ($J_{\text{PP}} = 187 \text{ Hz}$) for **22** and 28.6 and 91.0 ppm ($J_{\text{PP}} = 246 \text{ Hz}$) for **23**. A single-crystal X-ray diffraction study of **23** (Figure 5) re-

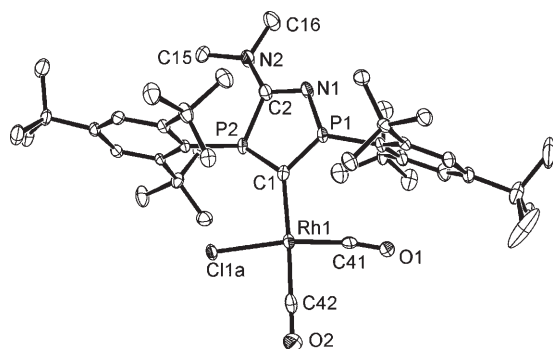


Figure 5. ORTEP view of the rhodium complex **23** (50% thermal ellipsoids shown). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–C41 1.822(4), Rh1–C42 1.878(4), Rh1–C1 2.111(3), P1–N1 1.629(3), P1–C1 1.668(4), P2–C1 1.756(3), P2–C2 1.827(4), O1–C41 1.148(5), O2–C42 1.144(5), N1–C2 1.337(5), N2–C2 1.344(5); C41–Rh1–C42 86.73(16), C41–Rh1–C1 95.87(15), C42–Rh1–C1 177.11(15), C42–Rh1–C1a 83.85(13), C1–Rh1–C1a 93.58(11), N1–P1–C1 112.53(16), N1–P1–C3 116.07(16), C1–P1–C3 126.06(17), C1–P2–C2 100.65(17), C1–P2–C9 125.30(16), C2–P2–C9 113.35(16), C2–N1–P1 110.5(2), C2–N2–C16 120.3(3), C2–N2–C15 124.8(3), C16–N2–C15 114.2(3), P1–C1–P2 101.61(18).

vealed a square-planar rhodium complex with a ligand structure reminiscent of resonance structure **5b'**; the N2 and P1 atoms are both nearly planar (sum of angles = 359.3° and 354.7°, respectively), and P2 remains pyramidal (339.4°). The carbonyl stretching frequencies of *cis*- $[\text{RhCl}(\text{CO})_2(\text{L})]$ complexes are generally recognized as an excellent measure of the σ -donor and π -acceptor properties of the ligand L.^[29] The observed values for both complexes **22** and **23** (2059, 1985 and 2062, 1981 cm^{-1} , respectively) are dramatically lower than those observed for the analogous complex **24**, which features the Enders NHC **E** as ligand (2089 and 2009 cm^{-1}) (Table 1). In fact, the observed values for **22** and **23** are as low as those reported for complexes that contain the most-basic NHC and even acyclic bis(amino)carbene ligands.^[30]

Conclusions

PHCs and their conjugate acids (PHCH^+ s) can be prepared and isolated only when the phosphorus atoms bear very bulky substituents, such as the 2,4,6-tris(*tert*-butyl)phenyl group; even *tert*-butyl groups do not allow for the preparation of the conjugate acids. The two synthetic routes described herein are applicable to various nitriles, which allows for some variation of the ring backbone. Of particular interest is dimethyl cyanamide, which can also be incorporated into the backbone, and the corresponding PHC has a zwitterionic structure that involves a tricoordinate pentavalent phosphorus atom. Both PHCs **D1** and **D2** are indefinitely stable in the solid state. In solution, **D2**, which comes from dimethyl cyanamide, is also stable in the absence of moisture, but **D1** made from acetonitrile undergoes a facile [3+2] cycloreversion. The reactivity of PHCs is strongly driven by the high electrophilicity of the phosphorus centers, as shown by their reactivity with water and benzaldehyde. PHCs **D1** and **D2** are direct analogues of the Enders carbene **E**, which is one of the less strongly basic NHCs. However, based on the carbonyl stretching frequencies of *cis*- $[\text{RhCl}(\text{CO})_2(\text{L})]$ complexes, the basicity of PHCs **D1** and **D2** appears comparable to those of the more-basic NHCs. Therefore, it is quite likely that saturated or even unsaturated PHCs without a nitrogen atom in the backbone would push upward the electronic parameter scale that characterizes NHC-type ligands.^[31] Moreover, we would expect such PHCs to be much less fragile than **D1** and **D2** because of the absence of the relatively weak phosphorus–nitrogen bond. The synthesis of such carbenes is under active investigation.

Experimental Section

General

All manipulations were performed under an inert atmosphere of dry argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H , ^{19}F , ^{13}C , and ^{31}P NMR spectra were recorded on

Bruker Avance 300 or Varian Inova 400 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported relative to SiMe_4 . ^{31}P and ^{19}F NMR chemical shifts are reported relative to 85% H_3PO_4 and CFCl_3 , respectively. FTIR spectra were recorded on a Bruker Equinox 55 spectrometer from KBr pellets.

Syntheses

3a: Compound **1** (0.80 g; 1.3 mmol) was dissolved in a mixture of dichloromethane (10 mL) and acetonitrile (2 mL, 38 mmol). One equivalent of GaCl_3 (0.235 g) in dichloromethane (2 mL) was added, with vigorous stirring, at -78°C . The reaction mixture was then warmed to room temperature. The solvents were removed under vacuum, and the crude product was crystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -30°C to give **3a** as white needles. Yield: 67%. M.p.: $173\text{--}175^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 298 K): $\delta = 1.39$ (s, 18H, CCH_3), 1.45 (s, 36H, CCH_3), 2.63 (dd, $J_{\text{PH}} = 2$, 20 Hz, 3H, NCCH_3), 7.73 (d, $^4J_{\text{PH}} = 4$ Hz, 2H, Ar), 7.75 (d, $^4J_{\text{PH}} = 3$ Hz, 2H, Ar), 8.60 ppm (dd, $^2J_{\text{PH}} = 7$, 16 Hz, 1H, PCHP); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298 K): $\delta = 22.2$ (dd, $J_{\text{PC}} = 25$, 30 Hz, NCCH_3), 30.8 (s, $\text{CH}_{3\text{para}}$), 30.9 (s, $\text{CH}_{3\text{para}}$), 33.0 (s, $\text{CH}_{3\text{ortho}}$), 33.4 (s, $\text{CH}_{3\text{ortho}}$), 38.5 (d, $J_{\text{PC}} = 3$ Hz, CCH_3), 38.6 (d, $J_{\text{PC}} = 8$ Hz, CCH_3), 119.3 (dd, $J_{\text{PC}} = 44$, 51 Hz, PCHP), 124.4 (d, $J_{\text{PC}} = 16$ Hz, Ar), 124.8 (d, $J_{\text{PC}} = 14$ Hz, Ar), 159.8 (d, $J_{\text{PC}} = 3$ Hz, Ar), 160.3 (d, $J_{\text{PC}} = 4$ Hz, Ar), 160.6 (dd, $J_{\text{PC}} = 3$, 13 Hz, Ar), 160.6 (d, $J_{\text{PC}} = 10$ Hz, Ar), 172.2 ppm (dd, $J_{\text{PC}} = 7$, 29 Hz, NCCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3 , 298 K): $\delta = 85$ ($^2J_{\text{PP}} = 266$ Hz), 104 ppm.

3b: A solid mixture of **1** (1.06 g, 1.7 mmol) and silver trifluoromethane sulfonate (0.453 g, 1.7 mmol) was cooled to -78°C . Acetonitrile (4 mL, 76 mmol) and dichloromethane (10 mL) were then added with vigorous stirring, and the reaction mixture was warmed to room temperature. After 30 min, the mixture was filtered and the solvent removed under vacuum. The crude product was crystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -30°C to give **3b** as white needles. Yield: 80%. M.p.: $157\text{--}159^\circ\text{C}$. The NMR data are identical to those of **3a**.

4a: Method A: Prepared in an identical manner to **3a**. The crude material was purified by crystallization from Et_2O cooled to -30°C . Yield: 76%. Method B: One equivalent of DBU was added to a solution of **11** (see below) (3.8 mmol) in CH_2Cl_2 (5 mL) cooled to -80°C . Upon warming to room temperature, the reaction was complete as ascertained by ^{31}P NMR spectroscopy. M.p.: $186\text{--}188^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 298 K): $\delta = 1.41$ (s, 18H, CCH_3), 1.42 (s, 9H, CCH_3), 1.43 (s, 9H, CCH_3), 1.50 (d, $^5J_{\text{PH}} = 1$ Hz, 18H, CCH_3), 7.30 (m, $^4J_{\text{PH}} = 5$ Hz, 5H, Ar), 7.64 (d, $^4J_{\text{PH}} = 5$ Hz, 2H, Ar), 7.80 (d, $^4J_{\text{PH}} = 4$ Hz, 2H, Ar), 8.70 ppm (dd, $^2J_{\text{PH}} = 6$, 18 Hz, 1H, PCHP); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298 K): $\delta = 31.6$ (s, $\text{CH}_{3\text{para}}$), 33.6 (s, $\text{CH}_{3\text{ortho}}$), 34.2 (s, $\text{CH}_{3\text{ortho}}$), 36.7 (d, $J_{\text{PC}} = 2$ Hz, CCH_3), 39.4 (d, $J_{\text{PC}} = 8$ Hz, CCH_3), 39.5 (d, $J_{\text{PC}} = 9$ Hz, CCH_3), 119.5 (dd, $J_{\text{PC}} = 57$, 62 Hz, PCHP), 125.1 (d, $J_{\text{PC}} = 20$ Hz, Ar), 126.2 (d, $J_{\text{PC}} = 18$ Hz, Ar), 127.8 (d, $J_{\text{PC}} = 11$ Hz, Ar), 130.0 (d, $J_{\text{PC}} = 2$ Hz, Ar), 132.8 (d, $J_{\text{PC}} = 6$ Hz, Ar), 134.5 (pt, $J_{\text{PC}} = 30$ Hz, Ar), 160 (m, Ar), 170.0 ppm (dd, $J_{\text{PC}} = 2$, 44 Hz, NCPH); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3 , 298 K): $\delta = 80$ (d, $^2J_{\text{PP}} = 240$ Hz), 106 ppm (d, $^2J_{\text{PP}} = 240$ Hz).

4b: Prepared in an identical manner to **3b**. The crude product was crystallized from Et_2O at -30°C to give **4b**. Yield: 85%. M.p.: 182°C (decomp.). The NMR data are identical to those of **4a**.

5b: A flask containing a solid mixture of **1** (500 mg, 0.832 mmol) and silver trifluoromethane sulfonate (0.214 g, 0.832 mmol) was cooled to -78°C . Dichloromethane (20 mL) and dimethylcyanamide (680 μL , 8.32 mmol) were added, and the solution was warmed to room temperature with stirring. After being stirred overnight, the yellow solution was filtered through a bed of celite to remove the AgCl precipitated, and the filtrate was dried in vacuo. The flask was then placed in an oil bath at 70°C overnight to remove excess dimethylcyanamide under vacuum. The remaining yellow powder was washed with hexanes (40 mL) and dried in vacuo. The material was crystallized from Et_2O (10 mL) at -30°C to give **5b** as yellow needles. Yield: 50%. M.p.: $118\text{--}122^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta = 1.31$ (s, 9H, CCH_3), 1.35 (s, 9H, CCH_3), 1.47 (s, 18H, CCH_3), 1.53 (s, 18H, CCH_3), 2.40 (brs, 3H, $\text{N}(\text{CH}_3)_2$), 3.22 (brs, 3H, $\text{N}(\text{CH}_3)_2$), 7.56 (d, $^4J_{\text{PH}} = 4$ Hz, 2H), 7.57 (d, $^2J_{\text{PH}} = 30$ Hz, 1H, PC(H)P), 7.69 ppm (d, 2H, $^4J_{\text{PH}} = 6$ Hz, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K): $\delta = 31.0$ (s, CCH_3), 31.1 (s, CCH_3), 33.5 (s, CCH_3), 33.7 (s, CCH_3),

33.8 (s, CCH_3), 35.7 (s, $\text{N}(\text{CH}_3)_2$), 36.2 (s, $\text{N}(\text{CH}_3)_2$), 39.0 (d, $J_{\text{PC}} = 3$ Hz, CCH_3), 39.3 (d, $J_{\text{PC}} = 4$ Hz, CCH_3), 115.4 (dd, $J_{\text{PC}} = 7.65$ Hz, PC(H)P), 121.0 (q, $J_{\text{FC}} = 320$ Hz, CF_3), 124.3 (Ar), 124.4 (Ar), 157.4 (d, $J_{\text{PC}} = 3$ Hz, Ar), 159.8 (brm, Ar), 160.7 (d, $J_{\text{PC}} = 4$ Hz, Ar), 160.9 (d, $J_{\text{PC}} = 4$ Hz, Ar), 178.9 (dd, $J_{\text{PC}} = 10$, 24 Hz, NCN); ^{19}F NMR (376 MHz, CDCl_3 , 298 K): 78.3 ppm (CF_3SO_3); ^{31}P NMR (162 MHz, CDCl_3 , 298 K): $\delta = 12.2$ (dd, $^2J_{\text{PP}} = 84$ Hz, $^2J_{\text{PH}} = 30$ Hz), 113.2 ppm (d, $^2J_{\text{PP}} = 284$ Hz).

11: A solution of $(\text{Mes}^*\text{PCl})_2\text{CH}_2$ **9** (1.27 g, 2 mmol) in CH_2Cl_2 (2 mL) and an excess of benzonitrile (2.06 g, 0.02 mol) was cooled to -80°C , whereupon GaCl_3 (0.352 g, 2 mmol, 1 equiv) was added. Upon warming to room temperature, the volatile solvents were removed in vacuo. Due to the highly unstable nature of this compound, the crude material was directly used in the next synthetic step, and complete spectroscopic characterization was not possible. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3 , 298 K): two diastereomers: $\delta = 71.1$, 106.1 ppm ($^2J_{\text{PP}} = 44$ Hz); 75.0, 109.5 ppm ($^2J_{\text{PP}} = 9$ Hz).

14: A solution of **12** (992 mg, 3.8 mmol) in CH_2Cl_2 (5 mL) and an excess of benzonitrile (7.83 g, 76 mmol) was cooled to -80°C , whereupon GaCl_3 (0.352 g, 2 mmol, 1 equiv) was added. Upon warming to room temperature, the mixture was stirred for six hours to yield a yellow solution. The volatile solvents were removed, and diethyl ether (40 mL) was added. Upon cooling to -30°C , a colorless powder precipitated. The powder was filtered, exhaustively washed with diethyl ether, and dried under vacuum to give **14**. Yield: 60%. ^1H NMR (200 MHz, CDCl_3 , 298 K): $\delta = 1.27$ (d, $^3J_{\text{PH}} = 15$ Hz, 9H, PCCH_3), 1.53 (d, $^3J_{\text{PH}} = 22$ Hz, 9H, PCCH_3), 2.99 (m, 1H, PCH_2P), 3.52 (m, 1H, PCH_2P), 7.63 ppm (m, 5H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3 , 298 K): $\delta = 103.2$ (s), 105.9 ppm (s).

15: A solution of **14** (378 mg, 0.7 mmol) in CH_2Cl_2 (5 mL) was cooled with stirring to -80°C , and DBU (1 equiv) was added. Upon warming to room temperature, the solution turned deep red in color. The volatile solvents were removed in vacuo, and the solids were extracted with pentane. Removal of pentane gave **15** as a red powder. Yield: 66%. ^1H NMR (200 MHz, CDCl_3 , 298 K): $\delta = 0.94$ (d, $^3J_{\text{PH}} = 13$ Hz, 9H, PCCH_3), 1.43 (d, $^3J_{\text{PH}} = 20$ Hz, 9H, PCCH_3), 2.26 (dd, $^2J_{\text{PH}} = 25$, 38 Hz, 1H, PCHP), 7.58 ppm (m, 5H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3 , 298 K): $\delta = 68.6$ (d, $^2J_{\text{PP}} = 9$ Hz), 112.7 ppm (d, $^2J_{\text{PP}} = 9$ Hz).

16: A stirred solution of **15** (730 mg, 2.5 mmol) in CH_2Cl_2 (5 mL) was cooled to -80°C , and GaCl_3 (440 mg, 1 equiv) was added. The reaction mixture was warmed to room temperature to give an orange-yellow solution. The solution was cooled to -10°C to yield yellow crystals. Due to the highly unstable nature of this compound, complete characterization was not possible. $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3 , 298 K): $\delta = 81.1$ (d, $^2J_{\text{PP}} = 19$ Hz), 153.8 ppm (d, $^2J_{\text{PP}} = 19$ Hz).

D1: A solution of **3b** (1 g, 1.4 mmol) in THF (5 mL) was cooled to -78°C , and a solution of lithium bis(trimethylsilyl)amide (0.335 g, 1.4 mmol) in THF (3 mL) was added dropwise. After warming to room temperature, the reaction was complete. The solvent was removed under vacuum, and the solid was extracted with pentane. The resulting solution was concentrated and cooled to -30°C to afford a yellow powder, which was dried under vacuum. Single crystals of **D1** suitable for X-ray analysis were obtained from a concentrated solution in THF/toluene cooled to -30°C . Yield: 72%. M.p.: $123\text{--}127^\circ\text{C}$; ^1H NMR (400 MHz, $[\text{D}_8]\text{THF}$; 263 K): $\delta = 1.35$ (s, 18H, CCH_3), 1.40 (s, 18H, CCH_3), 1.41 (s, 18H, CCH_3), 2.26 (dd, $J_{\text{PH}} = 3$, 13 Hz, 3H, NCCH_3), 7.61 (d, $^4J_{\text{PH}} = 4$ Hz, 2H, Ar), 7.63 ppm (d, $^4J_{\text{PH}} = 4$ Hz, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $[\text{D}_8]\text{THF}$, 263 K): $\delta = 19.8$ (dd, $J_{\text{PC}} = 30$, 34 Hz, $\text{N} = \text{CCH}_3$), 30.6 (s, CH_3), 32.0 (s, CH_3), 32.5 (s, CH_3), 35.3 (s, CCH_3), 38.3 (s, CCH_3), 121.1 (d, $J_{\text{PC}} = 34$ Hz, Ar), 121.3 (d, $J_{\text{PC}} = 34$ Hz, Ar), 122.3 (d, $J_{\text{PC}} = 12$ Hz, Ar), 122.5 (d, $J_{\text{PC}} = 11$ Hz, Ar), 153.8 (d, $J_{\text{PC}} = 4$ Hz, Ar), 153.9 (d, $J_{\text{PC}} = 3$ Hz, Ar), 157.8 (m, Ar), 179.1 (dd, $J_{\text{PC}} = 16$, 31 Hz, C=N), 184.4 ppm (pt, $J_{\text{PC}} = 147$ Hz, PCP); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $[\text{D}_8]\text{THF}$, 263 K): $\delta = 85$, 73 ppm ($^2J_{\text{PP}} = 135$ Hz).

D2: Salt **5b** (324 mg, 0.408 mmol) and lithium bis(trimethylsilyl)amide (68 mg, 0.408 mmol) were combined in a flask and cooled to -78°C , whereupon THF (5 mL) was added. The mixture was warmed to room temperature with stirring. After 30 min the solvent was removed in vacuo. The solids were extracted with hexanes (2×30 mL), and the hexane fractions were dried in vacuo to give **D2** as a light-yellow powder. Yield:

66%. Multiple crystals grown from a variety of solvents (THF, hexanes, benzene) suffered from twinning or severe disorder issues when analyzed by X-ray crystallography. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 1.30 (s, 18H, *p*-CCH₃), 1.73 (s, 18H, *o*-CCH₃), 1.77 (s, 18H, *o*-CCH₃), 2.49 (brs, 6H, N(CH₃)₂), 7.65 (d, $^4J_{\text{PH}}$ = 3 Hz, 2H, Ar-H), 7.74 ppm (d, $^4J_{\text{PH}}$ = 5 Hz, 2H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 31.6 (s, CCH₃), 31.7 (s, CCH₃), 33.9 (s, CCH₃), 39.4 (s, CCH₃), 39.7 (s, CCH₃), 40.4 (s, N-CCH₃), 122.9 (d, J_{PC} = 11 Hz, Ar), 123.1 (d, J_{PC} = 12 Hz, Ar), 153.6 (s, Ar), 154.3 (s, Ar), 158.6 (brm, Ar), 159.2 (brm, Ar), 186.6 (dd, J_{PC} = 52, 72 Hz, NCN), 187.3 ppm (dd, J_{PC} = 127, 153 Hz, PCP); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 298 K): δ = 13.7 (d, $^2J_{\text{PP}}$ = 232 Hz), 64.9 ppm (d, $^2J_{\text{PP}}$ = 232 Hz).

17: THF (10 mL) was added to a solid mixture of **3a** (500 mg, 0.6 mmol) and KH/*t*BuOK (80 mg, 1.6 mmol) (9:1). The reaction was monitored by ^{31}P NMR spectroscopy until completion, whereupon the solution was filtered and the volatile solvents removed in vacuo. The solid was crystallized from a cold solution in toluene to give 400 mg of **17**. Yield: 83%. M.p.: 253–255°C; ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 1.18 (s, 9H, CCH₃), 1.24 (s, 9H, CCH₃), 1.50 (s, 18H, CCH₃), 1.54 (s, 18H, CCH₃), 2.33 (dd, J_{PH} = 2, 18 Hz, 3H, NCCH₃), 7.70 (d, $^4J_{\text{PH}}$ = 6 Hz, 2H, Ar), 7.72 ppm (d, $^4J_{\text{PH}}$ = 6 Hz, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K): δ = 23.8 (dd, J_{PC} = 24, 29 Hz, NCCH₃), 29.1 (s, CH_{3para}), 31.6 (s, CH_{3ortho}), 39.4 (d, J_{PC} = 4 Hz, CCH₃), 39.6 (d, J_{PC} = 4 Hz, CCH₃), 124.5 (d, J_{PC} = 16 Hz, Ar), 125.2 (d, J_{PC} = 16 Hz, Ar), 157.9 (d, J_{PC} < 1 Hz, Ar), 159.0 (d, J_{PC} < 1 Hz, Ar), 160.0 (dd, J_{PC} = 5, 10 Hz, Ar), 160.5 (dd, J_{PC} < 1, 9 Hz, Ar), 174 ppm (d, J_{PC} = 25 Hz, NCCH₃) (the carbon atom attached to gallium was not observed, possibly owing the adjacent quadrupolar gallium nucleus); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 298 K): δ = 94 (d, $^2J_{\text{PP}}$ = 225 Hz), 114 ppm (d, $^2J_{\text{PP}}$ = 225 Hz).

18: THF (10 mL) was added to a rapidly stirring solid mixture of EtOK (89 mg, 1.1 mmol) and **4a** (1.02 g, 1.1 mmol) cooled to –80°C. After 1 h the mixture was warmed to room temperature, and the solution became dark purple. The solvent was removed in vacuo, and the solids were extracted with pentane (3 × 10 mL). Removal of pentane in vacuo gave **18** as an aquamarine powder. Yield: 600 mg, 70%. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 1.03 (s, 18H, CCH₃), 1.17 (t, J_{HH} = 7 Hz, OCCH₃), 1.29 (s, 9H, CCH₃), 1.31 (s, 9H, CCH₃), 1.80 (brs, 18H, CCH₃), 2.40 (dd, J_{PH} = 15, 35 Hz, 1H, PCHP), 3.73 (dq, J_{PH} = 57 Hz, J_{HH} = 7 Hz, 2H, OCH₂), 7.0–8.0 ppm (m, 9H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K): δ = 15.6 (s, OCCH₃), 27.7 (dd, J_{PC} = 7, 11 Hz, PCHP), 31.0 (s, CH₃), 31.1 (s, CH₃), 33.0 (m, CH₃), 34.5 (m, CCH₃), 39.0 (d, J_{PC} = 7 Hz, CCH₃), 59.0 (d, J_{PC} = 8 Hz, OCH₂), 119.3 (s, Ar), 122.0 (d, J_{PC} = 15 Hz, Ar), 123.0 (s, Ar), 127.8 (d, J_{PC} = 2 Hz, Ar), 129.3 (d, J_{PC} = 5 Hz, Ar), 129.9 (s, Ar), 131.9 (s, Ar), 137.9 (dd, J_{PC} = 19, 30 Hz, Ar), 149.2 (d, J_{PC} = 5 Hz, Ar), 152.0 (d, J_{PC} = 3 Hz, Ar), 157.0 (d, J_{PC} = 9 Hz, Ar), 160.4 (s, Ar), 160.8 (s, Ar), 193.4 ppm (dd, J_{PC} = 67, 144 Hz, N=C); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 298 K): δ = 44 (d, $^2J_{\text{PP}}$ = 57 Hz), 70 ppm (d, $^2J_{\text{PP}}$ = 57 Hz).

Hydrolysis of **D2**: H₂O (1 mL) was added to a freshly prepared solution of **D2** (3.82 mmol) in THF (10 mL) cooled to 0°C. After the mixture was stirred overnight, the volatile solvents were removed under vacuum. Dichloromethane (30 mL) was added, and the solution was dried with MgSO₄ and filtered. Removal of solvent in vacuo gave a yellow solid. Washing the solid with acetonitrile (2 × 5 mL) gave **20** as a white powder. Yield: 88%. Single crystals suitable for X-ray diffraction were obtained from a cooled solution in hexane. M.p.: 174–178°C; ^1H NMR (300 MHz, CHCl₃, 298 K, major isomer): δ = 0.67 (s, 9H, CCH₃), 1.20 (s, 9H, CCH₃), 1.29 (s, 9H, CCH₃), 1.56 (s, 18H, CCH₃), 1.61 (s, 9H, CCH₃), 1.84 (s, 3H, NCH₃), 2.99 (s, 3H, NCH₃), 3.04–3.22 (m, 2H, CH₂), 7.16–7.33 ppm (m, 4H, Ar); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CHCl₃, 298 K): major isomer: δ = –8.1, 56.8 ppm; minor isomer: δ = –20.3, 49.7 ppm (d, $^2J_{\text{PP}}$ = 11 Hz).

Reaction of **D1** with benzaldehyde: An excess of benzaldehyde (143 μL , 14 mmol) was added to a rapidly stirring solution of **D1** (0.850 g, 1.4 mmol) in THF (10 mL) cooled to –78°C. Upon warming to room temperature, the solvent was evaporated in vacuo. The residue was washed with pentane (5 mL) and then extracted with toluene (3 × 5 mL). Upon removal of toluene, **21** was obtained as a yellow powder. Yield: 37%. M.p.: 156–158°C; ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 1.13 (s, 9H, CCH₃), 1.14 (s, 9H, CCH₃), 1.29 (s, 9H, CCH₃), 1.58 (s, 9H, CCH₃),

1.58 (s, 18H, CCH₃), 2.18 (d, $^3J_{\text{PH}}$ = 7 Hz, 3H, NCCH₃), 6.72 (m, 3H, Ar), 7.00 (m, 2H, Ar), 7.30 (d, $^4J_{\text{PH}}$ = 4 Hz, 2H, Ar), 7.51 (d, $^4J_{\text{PH}}$ = 5 Hz, 2H, Ar), 8.50 (dd, J_{PH} = 13, 20 Hz, 1H, PC=CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K): δ = 26.7 (dd, J_{PC} = 23, 27 Hz, N=CCH₃), 30.8 (s, CCH₃), 30.9 (s, CCH₃), 33.1 (s, CCH₃), 33.8 (s, CCH₃), 34.2 (s, CCH₃), 34.5 (s, CCH₃), 39.3 (d, J_{PC} = 8 Hz, CCH₃), 118.5 (d, J_{PC} = 8 Hz, Ar), 119.1 (d, J_{PC} = 7 Hz, Ar), 122.3 (d, J_{PC} = 13 Hz, Ar), 122.8 (d, J_{PC} = 8 Hz, Ar), 128.1 (dd, J_{PC} = 10 Hz, J_{PC} = 25 Hz, HC=CP), 130.0 (Ar), 134.4 (dd, J_{PC} = 4 Hz, J_{PC} = 17 Hz, Ar), 141.1 (dd, J_{PC} = 48 Hz, J_{PC} = 84 Hz, PCP), 146.6 (m, Ar), 151.3 (d, J_{PC} = 4 Hz, Ar), 152.3 (d, J_{PC} = 3 Hz, Ar), 157.5 (d, J_{PC} = 8 Hz, Ar), 160.2 (dd, J_{PC} = 3 Hz, J_{PC} = 38 Hz, Ar), 160.2 (d, J_{PC} = 9 Hz, Ar), 193.5 ppm (d, J_{PC} = 41 Hz, N=C); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 298 K): δ = 0 (d, $^2J_{\text{PP}}$ = 77 Hz), 48 ppm (d, $^2J_{\text{PP}}$ = 77 Hz); MS (EI) (70 eV): m/z = 711 [M^+], 670 [$\text{M}-\text{NCCH}_3$]⁺, 613 [$\text{M}-\text{NCCH}_3-t\text{Bu}$]⁺, 557 [$\text{M}-\text{NCCH}_3-2t\text{Bu}$]⁺, 425 [$\text{M}-\text{NCCH}_3-\text{Ar}$]⁺, 57 [$t\text{Bu}$]⁺.

22 and **23:** A solution of **D1** or **D2** (0.8 mmol) in THF was added to a solution of the corresponding [(CO)₂RhCl]₂ complex (0.5 equiv) in THF at –78°C. After the mixture was warmed to room temperature and stirred overnight, the solvent was removed, and the remaining solids were extracted with hexanes (2 × 40 mL). The solvent was removed from the extracts in vacuo to give a light-brown powder. Crystallization from pentane/toluene at –30°C afforded **22** as yellow crystals, whereas crystallization from cooled toluene gave **23** as yellow crystals. **22:** Yield: 69%. M.p.: 175–178°C; IR (KBr): ν_{CO} = 1985, 2059 cm^{–1}; ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 1.23 (s, 9H, CCH₃), 1.26 (s, 9H, CCH₃), 1.60 (s, 18H, CCH₃), 1.62 (s, 18H, CCH₃), 2.33 (dd, J_{PH} = 4, 17 Hz, 3H, NCCH₃), 7.71 (d, $^4J_{\text{PH}}$ = 5 Hz, 2H, Ar), 7.74 ppm (d, $^4J_{\text{PH}}$ = 6 Hz, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K): δ = 22.2 (dd, J_{PC} = 25, 330 Hz, N=CCH₃), 31.5 (s, CH₃), 31.8 (s, CH₃), 34.6 (s, CH₃), 34.8 (s, CH₃), 36.2 (s, CCH₃), 36.0 (s, CCH₃), 40.0 (d, J_{PC} = 4 Hz, CCH₃), 40.6 (d, J_{PC} = 4 Hz, CCH₃), 116.3 (dd, J_{PC} = 11, 39 Hz, C_{arom}), 118.6 (dd, J_{PC} = 4, 58 Hz, C_{arom}), 124.6 (d, J_{PC} = 14 Hz, C_{arom}), 125.7 (dd, J_{PC} = 1, 14 Hz, C_{arom}), 156.2 (d, J_{PC} = 4 Hz, C_{arom}), 157.1 (d, J_{PC} = 3 Hz, C_{arom}), 159.0 (dd, J_{PC} = 5, 9 Hz, C_{arom}), 159.9 (dd, J_{PC} = 3, 9 Hz, C_{arom}), 175.9 (ddd, J_{PC} = 2, 8 Hz, $^1J_{\text{Rh,C}}$ = 24 Hz, CRh), 183.9 (ddd, $J_{\text{Rh,C}}$ = 75 Hz, J_{PC} = 3, 6 Hz, RhCO), 185.9 ppm (dt, $J_{\text{Rh,C}}$ = 86 Hz, J_{PC} = 3 Hz, RhCO); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 298 K): δ = 93, 101 ppm ($^2J_{\text{PP}}$ = 187 Hz). **23:** Yield: 61%. M.p.: 123–126°C; IR (KBr): ν_{CO} = 1981, 2062 cm^{–1}; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 1.22 (s, 9H, *p*-CCH₃), 1.25 (s, 9H, *p*-CCH₃), 1.73 (s, 18H, *o*-CCH₃), 1.74 (s, 18H, *o*-CCH₃), 2.43 (brs, 6H, N(CH₃)₂), 7.64 (d, $^4J_{\text{PH}}$ = 4 Hz, 2H, Ar), 7.72 ppm (d, $^4J_{\text{PH}}$ = 5 Hz, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ = 31.1 (CCH₃), 34.0 (CCH₃), 34.9 (CCH₃), 39.5 (d, J_{PC} = 3 Hz, NCH₃), 39.7 (CCH₃), 40.4 (d, J_{PC} = 3 Hz, NCH₃), 123.6 (d, J_{PC} = 14 Hz, C_{arom}), 125.1 (d, J_{PC} = 12 Hz, C_{arom}), 154.0 (d, J_{PC} = 3 Hz, C_{arom}), 156.0 (d, J_{PC} = 3 Hz, C_{arom}), 158.4 (m, C_{arom}), 182.1 (ddd, $^1J_{\text{Rh,C}}$ = 38 Hz, $^1J_{\text{PC}}$ = 3, 12 Hz, PCP), 183.7 (dd, $^1J_{\text{Rh,C}}$ = 72 Hz, $^2J_{\text{PC}}$ = 4 Hz, RhCO), 185.5 (dd, $^1J_{\text{Rh,C}}$ = 58 Hz, $^3J_{\text{PC}}$ = 6 Hz, RhCO) (N=C=N carbon signal not detected possibly owing to adjacent quadrupolar nitrogen atoms and multiple P–C couplings); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K): δ = 28.6 (dd, $^2J_{\text{PP}}$ = 246 Hz, $^2J_{\text{Rh,P}}$ = 5 Hz), 91.0 (d, $^2J_{\text{PP}}$ = 246 Hz).

Crystal-Structure Determination

A Bruker X8-APEX X-ray diffraction instrument with Mo radiation was used for data collection for **5b**, **20**, and **23**. Data frames were collected at low temperature (100 K) by using the ω -, ϕ -scan modes (0.3° ω -scan width, hemisphere of reflections). A Bruker SMART-1000 X-ray diffraction instrument with Mo radiation was used for data collection for **16** and **17** at 133 and 193 K, respectively. All data frames were collected with the ω -scan mode (–0.3° ω -scan width, hemisphere of reflections). Intensity data were corrected for Lorentzian polarization, and absorption corrections were performed with the SADABS program. Data integration was performed with the Bruker SAINTPLUS software package version 7.21 A for **5b**, **20**, and **23** and version 5.02 for **16** and **17**. The SIR92 program was used for direct methods of phase determination for solutions of **5b**, **20**, and **23**, and the Bruker SHELXTL software package was used for **16** and **17**. Bruker SHELXTL software package version 6.14 for **5b**, **20**, and **23** and version 6.10 for **16** and **17** were used for structure refinement and difference Fourier maps. Atomic coordinates and isotropic and anisotropic displacement parameters of all non-hydrogen atoms were

refined by means of a full-matrix least-squares procedure on F^2 . All H atoms were included in the refinement in calculated positions riding on the C atoms, with U_{iso} fixed at 20% higher than the isotropic parameters of the carbons atoms to which they were attached. Ortep diagrams were produced with Ortep 3. CCDC-619517 (**5b**), -619518 (**16**), -619519 (**17**), -619520 (**20**), and -619521 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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- [1] For general reviews on stable carbenes: a) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; b) W. Kirmse, *Angew. Chem.* **2004**, *116*, 1799; *Angew. Chem. Int. Ed.* **2004**, *43*, 1767; c) R. W. Alder, M. E. Blake, M. E. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020; *Angew. Chem. Int. Ed.* **2004**, *43*, 5896; d) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857; e) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
- [2] For reviews on stable carbenes as ligands for transition metal catalysts: a) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815; b) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829; c) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; d) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247; e) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; f) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534; g) M. C. Perry, K. Burgess, *Tetrahedron: Asymmetry* **2003**, *14*, 951; h) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; i) L. Jafarpour, S. P. Nolan, *Adv. Organomet. Chem.* **2001**, *46*, 181; j) D. Enders, H. Gielen, *J. Organomet. Chem.* **2001**, *617–618*, 70.
- [3] For examples, see: a) E. Despagne, K. Miqueu, H. Gornitzka, P. W. Dyer, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2002**, *124*, 11834; b) X. Cattoën, H. Gornitzka, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1342; c) V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670; d) K. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *649*, 219; e) N. Merceron-Saffon, H. Gornitzka, A. Baceiredo, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 1431.
- [4] a) W. A. Herrmann, K. Ofele, D. von Preysing, E. Herdtweck, *J. Organomet. Chem.* **2003**, *684*, 235; b) W. W. Schoeller, D. Eisner, S. Grigoleit, A. R. Rozhenko, A. Alijah, *J. Am. Chem. Soc.* **2000**, *122*, 10115.
- [5] a) V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705; b) V. Lavallo, Y. Canac, A. Dehope, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236.
- [6] a) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722; b) V. Lavallo, Y. Ishida, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2006**, *118*, 6804; *Angew. Chem. Int. Ed.* **2006**, *45*, 6652.
- [7] J. Kapp, C. Schade, A. M. El-Nahasa, P. von R. Schleyer, *Angew. Chem.* **1996**, *108*, 2373; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2236.
- [8] L. Nyulászi, *Tetrahedron* **2000**, *56*, 79.
- [9] For calculations on PHCs, see: a) A. Fekete, L. Nyulászi, *J. Organomet. Chem.* **2002**, *643–644*, 278; b) W. W. Schoeller, D. Eisner, *Inorg. Chem.* **2004**, *43*, 2585; c) H. Jacobsen, *J. Organomet. Chem.* **2005**, *690*, 6068.
- [10] A titanocene and a zirconocene complex of a PHC have already been spectroscopically characterized: T. Cantat, N. Mézailles, N. Maigrot, L. Ricard, P. Le Floch, *Chem. Commun.* **2004**, 1274.
- [11] A trimethylalane adduct of a cyclic anion with a diphosphinocarbene unit has been isolated: E. Niecke, A. Fuchs, M. Nieger, O. Schmidt, W. W. Schoeller, *Angew. Chem.* **1999**, *111*, 3216; *Angew. Chem. Int. Ed.* **1999**, *38*, 3031.
- [12] Metalladiphosphinocarbenes are known as transient species: J. Ruiz, M. E. G. Mosquera, G. García, E. Patrón, V. Riera, S. García-Granda, F. Van der Maelen, *Angew. Chem.* **2003**, *115*, 4915; *Angew. Chem. Int. Ed.* **2003**, *42*, 4767.
- [13] Several bis(iminophosphoranyl)carbene $[(R_2P=NSiMe_3)_2C]$ complexes have been isolated: N. D. Jones, G. Lin, R. A. Gossage, R. McDonald, R. G. Cavell, *Organometallics* **2003**, *22*, 2832.
- [14] A preliminary communication on this work: D. Martin, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2005**, *117*, 1728; *Angew. Chem. Int. Ed.* **2005**, *44*, 1700.
- [15] Acyclic diphosphaallyl cations of type $[>P-C(R)-P<]^+$ are unstable towards rearrangement: a) T. Kato, H. Gornitzka, A. Baceiredo, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2002**, *124*, 2506; b) T. Kato, H. Gornitzka, A. Baceiredo, W. W. Schoeller, G. Bertrand, *Science* **2000**, *289*, 754.
- [16] Only one four- and one five-membered C-substituted ($R=SiMe_3$) derivatives are known: a) M. Sebastian, O. Schmidt, A. Fuchs, M. Nieger, D. Szieberth, L. Nyulaszi, E. Niecke, *Phosphorus Sulfur Silicon Relat. Elem.* **2004**, *179*, 779; b) A. Fuchs, M. Nieger, E. Niecke, L. Nyulaszi, O. Schmidt, W. Schoeller, M. Sebastian, *Phosphorus Sulfur Silicon Relat. Elem.* **2002**, *177*, 1605; c) M. Sebastian, A. Hoskin, M. Nieger, N. Nyulaszi, E. Niecke, *Angew. Chem.* **2005**, *117*, 1429; *Angew. Chem. Int. Ed.* **2005**, *44*, 1405.
- [17] a) H. H. Karsch, H. U. Reisacher, G. Muller, *Angew. Chem.* **1986**, *98*, 467; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 454; b) H. H. Karsch, H. Reisacher, T. Ruprich in *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 3 (Ed.: W. A. Hermann), Thieme Verlag, Stuttgart, **1996**, pp. 140.
- [18] a) A. H. Cowley, R. A. Kemp, *Chem. Rev.* **1985**, *85*, 367; b) A. H. Cowley, *ACS Symp. Ser.* **2006**, *917*, 2; c) N. Burford, P. J. Ragogna, *ACS Symp. Ser.* **2006**, *917*, 280.
- [19] H. H. Karsch, F. H. Köhler, H. Reisacher, *Tetrahedron Lett.* **1984**, *25*, 3687.
- [20] A. A. Prishchenko, Z. S. Novikova, J. F. Lutsenko, *Z. Obshch. Khim.* **1980**, *50*, 689.
- [21] a) A. Stasch, S. Singh, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *Eur. J. Inorg. Chem.* **2004**, 4052; b) A. Beste, O. Krämer, A. Gerhard, G. Frenking, *Eur. J. Inorg. Chem.* **1999**, 2037; c) A. H. Cowley, F. P. Gabbaï, C. J. Carrano, L. M. Mokry, M. R. Bond, G. Bertrand, *Angew. Chem.* **1994**, *106*, 584; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 578.
- [22] a) A. Igau, A. Baceiredo, H. Grützmacher, H. Pritzkow, G. Bertrand, *J. Am. Chem. Soc.* **1989**, *111*, 6853; b) O. Guerret, G. Bertrand, *Acc. Chem. Res.* **1997**, *30*, 486; c) H. Grützmacher, H. Pritzkow, *Angew. Chem.* **1991**, *103*, 721; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 709; d) G. Frenking, S. Fau, C. M. Marchand, H. Grützmacher, *J. Am. Chem. Soc.* **1997**, *119*, 6648; e) H. Grützmacher, C. M. Marchand, *Coord. Chem. Rev.* **1997**, *163*, 287.
- [23] a) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, F. Knock, *Angew. Chem.* **1984**, *96*, 621; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 619; b) H. H. Karsch, H. U. Reisacher, G. Muller, *Angew. Chem.* **1984**, *96*, 619; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 618; c) H. H. Karsch, F. H. Köhler, H. U. Reisacher, *Tetrahedron Lett.* **1984**, *25*, 3687; d) M. Yoshifuji, K. Toyota, N. Inamoto, *J. Chem. Soc. Chem. Commun.* **1984**, 689; e) H. H. Karsch, A. Appelt, H. U. Reisacher, G. Müller, *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 417; f) M. Yoshifuji, S. Sasaki, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 839; g) M. Gouygou, M. Koenig, J. Escudé, C. Couret, *Heteroat. Chem.* **1991**, *2*, 221; h) M. Yoshifuji, S. Sasaki, T. Niitsu, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 187; i) M. Yoshifuji, S. Sasaki, N. Inamoto, *J. Chem. Soc. Chem. Commun.* **1989**, 1732.

- [24] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, 107, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1021.
- [25] M. K. Denk, J. M. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, 617, 242.
- [26] For examples, see: a) R. Breslow, *J. Am. Chem. Soc.* **1958**, 80, 3719; b) D. Enders, O. Niemeier, T. Balensiefer, *Angew. Chem.* **2006**, 118, 1491; *Angew. Chem. Int. Ed.* **2006**, 45, 1463; c) H. Takikawa, Y. Hachisu, J. W. Bode, K. Suzuki, *Angew. Chem.* **2006**, 118, 3572; *Angew. Chem. Int. Ed.* **2006**, 45, 3492; d) M. S. Kerr, J. R. de Alaniz, T. Rovis, *J. Org. Chem.* **2005**, 70, 5725; e) C. Burstein, F. Glorius, *Angew. Chem.* **2004**, 116, 6331; *Angew. Chem. Int. Ed.* **2004**, 43, 6205; f) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, 37, 534; g) J. Pesch, K. Harms, T. Bach, *Eur. J. Org. Chem.* **2004**, 9, 2025.
- [27] a) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, 110, 6463; b) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem.* **1989**, 101, 617; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 621; c) T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* **2000**, 122, 998.
- [28] a) O. Illa, H. Gornitzka, V. Branchadell, A. Baceiredo, G. Bertrand, R. M. Ortuno, *Eur. J. Org. Chem.* **2003**, 3147; b) O. Illa, H. Gornitzka, A. Baceiredo, G. Bertrand, V. Branchadell, R. M. Ortuno, *J. Org. Chem.* **2003**, 68, 7707.
- [29] M. Mayr, K. Wurst, K. H. Ongania, M. Buchmeiser, *Chem. Eur. J.* **2004**, 10, 1256.
- [30] a) R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem.* **1996**, 108, 1211; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1121; b) K. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, 649, 219.
- [31] For computational considerations on new metathesis catalysts based on PHCs, see: a) W. W. Schoeller, D. Schroeder, A. B. Rozhenko, *J. Organomet. Chem.* **2005**, 690, 6079; b) H. Jacobsen, *Dalton Trans.* **2006**, 18, 2214; c) G. Occhipinti, H. R. Bjorsvik, *J. Am. Chem. Soc.* **2006**, 128, 6952.

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