Organophosphorus Compounds, 118[◇]

Reactions of 1-Chloro-1*H*-phosphirenes with Nucleophiles

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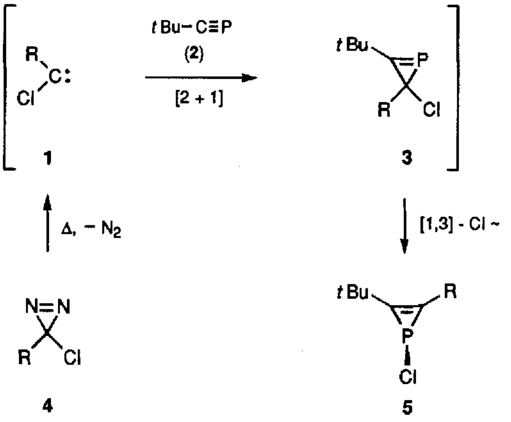
The halogen atoms in the 1-chloro-1*H*-phosphirenes, **5a–c**, are easily substituted on reaction with organolithium and Grignard reagents, **14a–p**, with formation of the corresponding *O*-, *N*-, *C*-, *Si*-, and *Ge*-substituted 1*H*-phosphirenes, **15a–t**. Cl/H exchange reactions also occur on reaction with lithium metal hydrides (**5a** → **17**). Furthermore, substitution reactions are also realized with the alkali metal borates, **18a–g** (→**19a–g**); the same is true for reactions with trimethylsilyl cyanide and azide (→**22a–d**). Some of the substitution products have been characterized in the form of their metal complexes, **16**, **23**, **24**, and **25**.

Introduction

Only a few years ago, unsaturated heterocyclic three-membered ring systems containing $\lambda^3\sigma^3$-phosphorus atoms (1*H*-phosphirenes) were considered as curiosities; however, as a result of the pioneering work of F. Mathey, they have now been recognized as easily accessible and versatile building blocks in organoelement chemistry[2,3,4]. In contrast, the chemistry of unsaturated heterocyclic three-membered ring systems containing $\lambda^3\sigma^2$-phosphorus atoms (2*H*-phosphirenes) has not yet been fully explored[5]. By analogy with the synthesis of cyclopropenes by [2 + 1] cycloaddition of carbenes to alkynes, the application of the same cycloaddition process to phosphaalkynes appeared to provide a logical approach for the study of this class of compounds. These expectations were further strengthened by the discovery of the pronounced ability of phosphaalkynes[6–10] to participate in cycloaddition reactions[11].

When the chlorocarbenes, **1** are generated by thermal decomposition of the diazirines, **4**, in the presence of 2,2-dimethylpropylidynephosphane (**2**; *tert*-butylphosphaacetylene)[12], the expected 2*H*-phosphirenes, **3**, cannot be isolated; instead, the corresponding 1*H*-isomers, **5**, are obtained[13,14].



1,3 - 5	a	b	c
R	Ph	*t*Bu	OEt

The isomerization, **3** → **5**, proceeds through a [1,3] chlorine shift from carbon to phosphorus and is powered by elimination of the thermodynamically unfavorable C–P double bond in the 2*H*-phosphirenes. 1*H*-Phosphirenes, such as **5**, do not exhibit any antiaromatic behavior because the high barrier to inversion at phosphorus prevents the intermediacy of an antiaromatic, planar transition-state.

1-Chloro-1*H*-phosphirene (**5a**) exhibits a high reactivity towards both electrophilic and nucleophilic reagents.

Compound **5** reacts with water to furnish the vinylphosphonous acid **6**[14]. The chlorine atom can be exchanged for fluorine by reaction with silver tetrafluoroborate (→**7**)[14] and for bromine[14], iodine[14], or azide[13] (→**8**) by treat-

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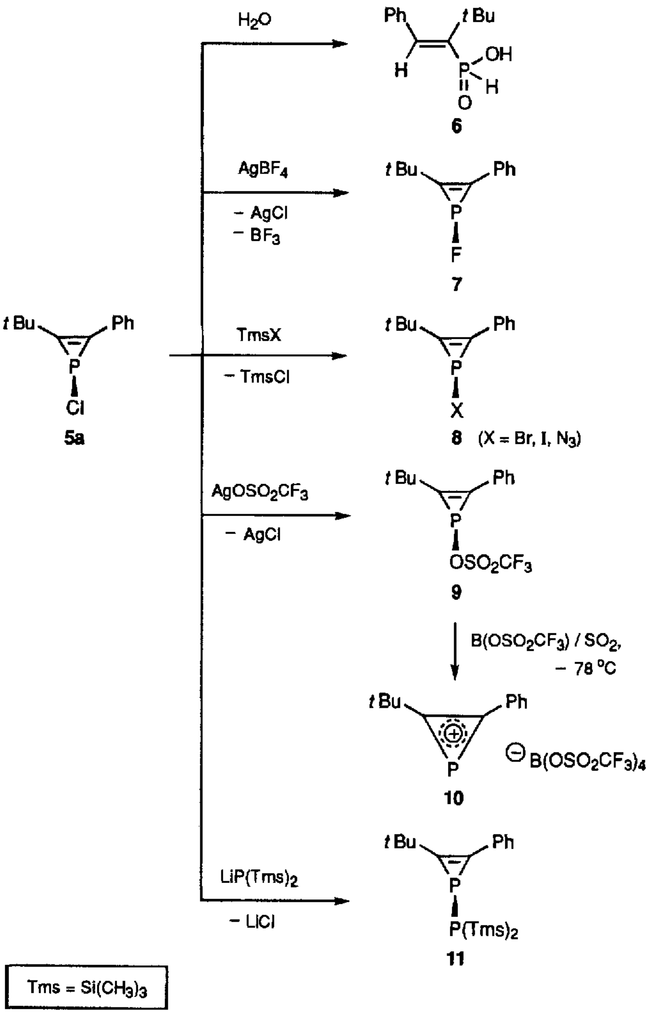
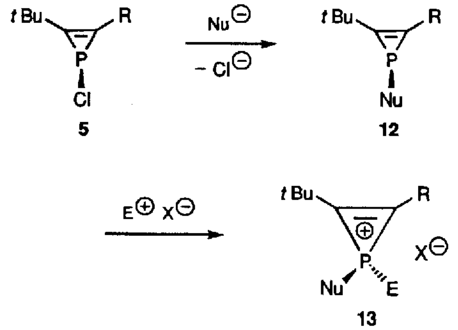


ment with trimethylsilyl halides or azide. The exchange of the chlorine atom in **5a** for a trifluoromethanesulfonyloxy group (→**9**) provides the starting point for an interesting reaction sequence. On treatment of **9** with sulfur dioxide in the super Lewis acid tris(trifluoromethylsulfonyloxy)borane, the trifluoromethanesulfonyloxy group is eliminated to furnish the first ever phosphirenylium cation, **10**, which can then be spectroscopically investigated in solution[15]. P–P bond formation occurs when **5a** is allowed to react with lithium bis(trimethylsilyl)phosphane[13]. This reaction (→**11**) gives rise to a functionally substituted 1*H*-phosphirene suitable for furhter transformations.



In the present work we have examined the nucleophilic substitution reactions of the chlorine atom in 1-chloro-1*H*-phosphirene (**5a**) in detail by using a wide variety of nucleophiles. Furthermore, some subsequent reactions of the obtained substitution products, **12**, are included.

One interesting question, which will be the subject of a separate report, is whether the 1*H*-phosphirenes, **12**, will react with electrophiles to furnish the phosphirenium salts, **13**[16]. Theoretical calculations predict the presence of σ^*-aromaticity for the latter species[17].

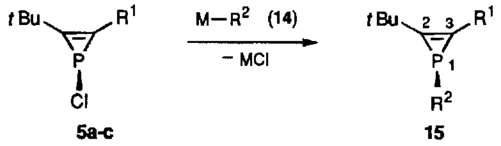
Results

Reactions of 5 with Lithium and Grignard Nucleophiles, 14a–p

When the 1-chloro-1*H*-phosphirenes, **5a**–**c**, were allowed to react with a variety of different nucleophiles, **14**, smooth nucleophilic replacement of the chlorine atom bonded to phosphorus with formation of the novel 1*H*-phosphirenes, **15a**–**t**, was observed in every case. Oxygen- (**14a**), nitrogen- (**14b**–**d**), carbon- (**14e**–**n**), silicon- (**14o**), and germanium-nucleophiles (**14p**) could be employed in the form of the corresponding lithium salts or Grignard reagents. Most impressive, above all, is the wide range of carbon-nucleophiles that could be used, ranging from alkyl- (**14e**–**g**), aryl- (**14h**), vinyl- (**14i**), and alkynyl-substituted species (**14j**), through to the functionally-substituted alkyl reagents (**14k**–**n**).

The 1*H*-phosphirenes, **15a**–**t**, were obtained in moderate to very good yields (35–90%), usually after bulb-to-bulb distillation, as colorless to pale yellow liquids. Exceptions are **15j**, **15q**, and **15r** which were isolated as waxy crystals which slowly deliquesced at room temperature. All products were sensitive to moisture and a few also to temperature so that satisfactory elemental analyses could not be recorded for some of the products. However, the spectroscopic data are unambiguous and fully support the given constitutions for the three-membered ring heterocyclic products.

The ^{31}P-NMR signals for the phosphorus atom in the three-membered ring appeared at relatively high-field between $\delta = -71.1$ and -228. This is readily understandable since the inherent ring strain and the geometry of the heterocyclic system implies a chemical shift range in the direction of that of white phosphorus ($\delta = -488$). Of course, the nature of the substituent at phosphorus ($EN = 2.19$[18]) also has a decisive influence of the position of the signal. Accordingly, signals for phosphorus atoms bonded to the electronegative heteroatoms, oxygen ($EN = 3.55$) and nitrogen ($EN = 3.04$), of the substituted 1*H*-phosphirenes, **15a**–**e**, appeared in the low-field part of the shift range ($\delta = -71.1$ to -127.2), while the 1*H*-phosphirenes, **15q**–**t**, with the electropositive elements silicon ($EN = 1.90$) and germanium ($EN = 2.01$) bonded to phosphorus occurred in the high-field part ($\delta = -139.6$ to -203.5). The carbon ($EN = 2.55$) substituted 1*H*-phosphirenes, **15f**–**p**, exhibited signals between $\delta = -122.7$ and -228.0; here it is conspicuous that unsaturated groups affect a pronounced shift to higher field. The chemical shift values determined for the remaining 1*H*-phosphirenes were within this observed range[19].



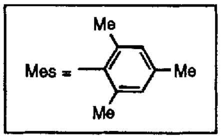
14	a	b	c	d	e	f	g	h	i	j
R^2	OMe	NEt_2	$N\textit{i}Pr_2$	$NTms_2$	Me	Et	*t*Bu	Mes	$-CH=CH_2$	$-C\equiv C-\textit{t}Bu$
M	Li	Li	Li	Li	Li	MgBr	Li	MgBr	MgBr	Li

14	k	l	m	n	o	p
R^2	CH_2Tms	$CHTms_2$	$CTms_3$	$C(=N_2)Tms$	$SiTms_3$	$GeTms_3$
M	MgCl	Li	Li	Li	Li	Li

15	a	b	c	d	e	f	g	h	i	j
R^1	Ph	*t*Bu	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph
R^2	OMe	OMe	NEt_2	$N\textit{i}Pr_2$	$NTms_2$	Me	Et	*t*Bu	Mes	$-CH=CH_2$

15	k	l	m	n	o	p	q
R^1	Ph	Ph	Ph	Ph	Ph	*t*Bu	Ph
R^2	$-C\equiv C-\textit{t}Bu$	CH_2Tms	$CHTms_2$	$CTms_3$	$C(=N_2)Tms$	$C(=N_2)Tms$	$SiTms_3$

15	r	s	t
R^1	*t*Bu	OEt	Ph
R^2	$SiTms_3$	$SiTms_3$	$GeTms_3$



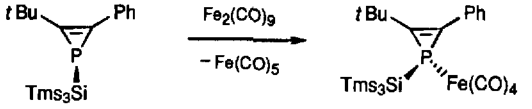
The ^{13}C-NMR values for the carbon atoms of the phosphirene double bond are characteristic of their environment. The signals for both carbon atoms appeared as doublets with $^1J_{C,P}$ coupling constants of 40−70 Hz. It is worthy of mention that for the nonsymmetrically substituted 1*H*-phosphirenes, **15a**, **c**−**o**, **q**, and **t** (R^1 = Ph), the signal for carbon atom C-2 was shifted downfield by 17−23 ppm in comparison to that of carbon atom C-3[20]. Furthermore, the absolute value for the $^1J_{C,P}$ = coupling constant for the C-2 signal was up to 14 Hz larger than the corresponding coupling constant for C-3. The 1*H*-phosphirene, **15s**, with an ethoxy substituent at C-3, constitutes an exception to this trend. In this compound, the signal for C-3 was shifted downfield by 48 ppm in comparison to that of C-2 and the $^1J_{C\text{-}3,P}$ coupling was 12 Hz larger than the corresponding coupling for C-2; these observations confirm the existence of an electron-rich enol ether double bond as a structural increment of **15s**. In the 1*H*-phosphirenes, **15f**−**p**, the signal for the exocyclic carbon atom bonded to the phosphirene phosphorus atom depended on the nature of the substituents, and, with the exception of **15h**, appeared as a doublet with $^1J_{C,P}$ couplings that were larger than the endocyclic $^1J_{C,P}$ couplings. The largest coupling constants (>100 Hz) were found for the derivatives **15k** and **15n** with the alkynyl and tris(trimethylsilyl)methyl substituents, respectively, since the coupling constants increase with increasing *s* character of the carbon atom bonded to phosphorus[21]. The remaining ^{13}C-NMR chemical shifts for the investigated 1*H*-phosphirenes were directly comparable with those of other 1-alkyl-[22] and 1-aryl-1*H*-phosphirenes[23].

The ^{1}H-NMR spectrum of **15j**, in which the 1-vinyl substituent is bonded to phosphorus, also deserves mention. Together with the phosphorus atom, the vinyl protons form an ABCX spin system that can be completely solved and simulated for the ABC part[24] (for details, see Experimental Section). The data were in agreement with those of other vinylphosphanes[25].

With regard to the mechanism, we assume that substitution of chlorine by the employed nucleophile proceeds in two steps. Firstly, a phosphirenide anion is formed by addition of the nucleophile to the phosphirene phosphorus atom; in the second step, cleavage of the metal chloride then leads to the final product. Indirect support for this hypothesis is provided by the detection of a corresponding intermediate in reactions of the phosphiranes with organolithium reagents[26,27]. An S_N2-type substitution, which is mechanistically preferred in nucleophilic substitution reactions of other halophosphanes[28], or heterolytic cleavage of **5** to give a phosphirenylium cation with subsequent substitution according to an S_N1 process, are highly improbable under the chosen reaction conditions.

Interesting reactions are to be expected for the 1*H*-phosphirenes, **15o** and **p**, which possess a highly reactive diazomethyl group bonded to the phosphirene phosphorus atom. By analogy with the formation of cyclobutadienes via the well-known ring expansion reactions of (diazomethyl)cyclopropenes[29,30], these compounds could provide an access route to the previously unknown phosphacyclobutadienes (phosphetes). However, to date, all attempts to prepare phosphetes by this route have been unsuccessful[31]. An interesting rearrangement is observed on photolysis of 2-tris(trimethylsilyl)silyl-1*H*-phosphirene (**15q**); this reaction leads to the 1,2-dihydro-1,2-phosphasilete by way of ring expansion and migration of a trimethylsilyl group from silicon to phosphorus[32,33].

As already mentioned, structural confirmation of the extremely hydrolysis-sensitive 1*H*-phosphirenes, **15**, has been achieved in some cases by formation of metal complexes; thus, the silyl derivative **15q** was treated with enneacarbonyldiiron to furnish the crystalline, analytically pure, η^1-iron complex, **16**, in 50% yield.

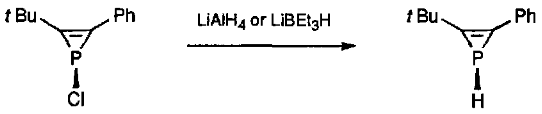


15q **16**

These complexations were accompanied by paramagnetic shifts of the signals of the ring atoms both in the ^{31}-NMR spectra ($\delta = -205.5 \rightarrow -141.0$) and in the ^{13}C-NMR spectra (C-2: $\delta = 130.9 \rightarrow 143.2$; C-3: $\delta = 115.5 \rightarrow 127.8$). At the same time, both $^1J_{C,P}$ coupling constants were reduced by about 20 Hz. This behavior is typical for complexed 1*H*-phosphirenes and has been reported previously[34,35].

Reactions of 5 with Complex Hydrides

The above-mentioned reactions of **5** with nucleophiles pose the question of whether unsubstituted 1*H*-phosphirenes could be accessed by the corresponding reactions with hydride ions. A *P*-unsubstituted 1*H*-phosphirene, complexed with a pentacarbonyltungsten fragment, has been described[22]. However, sodium borate (borohydride) in diethyl ether does not react with **5a** and when a mixture of methanol/diethyl ether was used as the solvent for this reaction, exchange of the chlorine atom for a methoxy group occurred, furnishing the already described product, **15a** (yield: 85%)[24]. We can therefore assume that a methoxyborate is initially formed, which then transfers a methoxy group to the phosphirene phosphorus atom (see also the next section). Replacement of sodium borohydride by the considerably more reactive lithium borohydride, however, did enable the preparation of the first non-complexed, *P*-unsubstituted 1*H*-phosphirene, **17**, in 76% yield. Compound **17** could also be obtained from the reactions of **5a** with tributyltin hydride in chloroform[24] or lithium triethylborate ("superhydride")[36] in THF/diethyl ether[37].

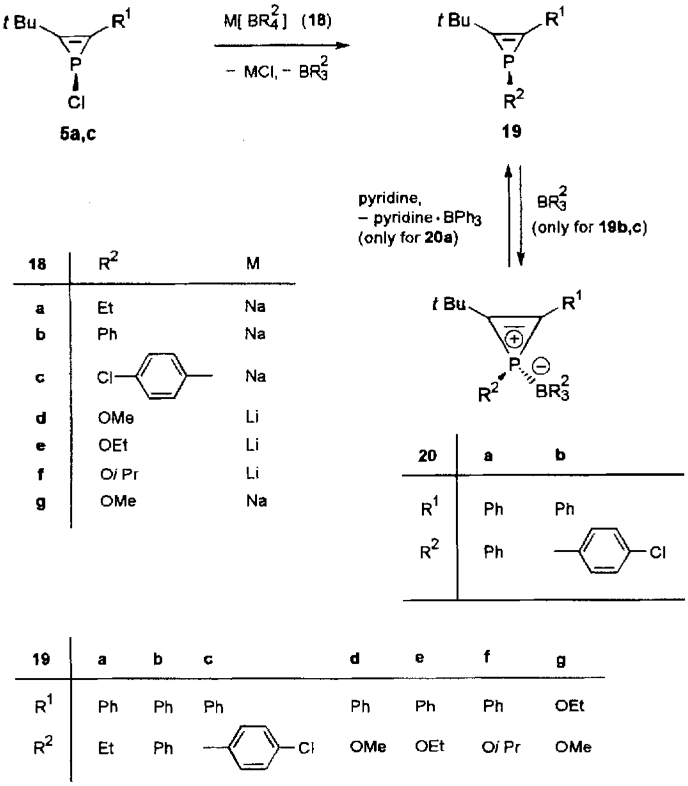


5a **17**

Thermally, the phosphirene, **17**, is rather unstable; the compound even decomposed in solution to furnish 3,3-dimethyl-1-phenylbut-1-yne (*t*Bu−C≡C−Ph) and a phosphinidene fragment [H−P]; the fate of the latter species is still unknown. The alkyne was obtained specifically in 58% yield by bulb-to-bulb distillation of **17**. In spite of this thermolability, the phosphirene, **17**, has been unambiguously characterized by its spectroscopic data and by its chemical reactions. A conspicuous feature of the ^{31}P-NMR spectrum was the extremely high-field position of the phosphorus signal at $\delta = -247.1$. The pronounced *s*-character of the free electron pair at the phosphorus atom and the resultant strong shielding is assumed to be the reason for this. The accompanying high *p*-character of the P−H bond resulted in an extremely small $^1J_{P,H}$ coupling constant of 107.0 Hz[38,39]. In the ^{13}C-NMR spectrum the ring carbon atoms gave rise to doublet signals in the expected regions (C-2: $\delta = 126.8$, C-3: $\delta = 108.1$) with $^1J_{C,P}$ coupling constants of 39.2 and 45.6 Hz, respectively. In comparison to the 1*H*-Phosphirenes, **15**, both signals were shifted by about 20 ppm to higher field. Thus, both the ^{31}P- and the ^{13}C-NMR data for **17** lay in the uppermost high-field range of all investigated 1*H*-phosphirenes. The bond parameters derived from the spectroscopic data − high *s*-nature of the free electron pair at phosphorus and high *p*-proportion of the P−H bond − indicate that the phosphorus atom exhibits a certain degree of phosphide anion character and that the hydrogen bonded to phosphorus will reflect protic properties. Indeed, the former effect accounts for the instability of **17** by way of antiaromatic interactions in the ring, while the latter effect can be exploited preparatively to convert **17** to 1-acyl-1*H*-phosphirenes by reaction with acyl chlorides in the presence of a base[37].

Reactions of 5 with Sodium and Lithium Borates, 18a−g

As mentioned in the preceding section, reaction of **5a** with sodium borohydride in methanol/diethyl ether resulted in smooth replacement of the chlorine atom by a methoxy group. This observation prompted us to investigate systematically the behavior of 1-chloro-1*H*-phosphirenes towards borates. In fact, **5a** does readily react with the lithium or sodium salts of alkyl-, aryl-, and alkoxyborates. In the cases of the arylborates, **18b**, and **c**, the substitution reaction was directly followed by a Lewis acid/Lewis base adduct formation in which the triarylborane added to the formed 1-aryl-1*H*-phosphirene **19** (→**20b**, **c**)[40]. However, when the Lewis base pyridine was added directly to **5a** and **18b**, or to a chloroform solution of **20b**, it released the phosphirene moiety, and the free 1-aryl-phosphirene, **19b**, was isolated without difficulty.



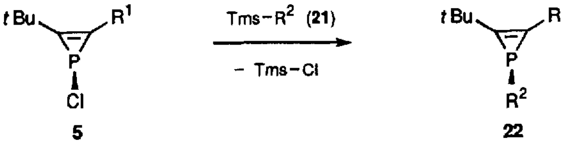
The fact that **20b** and **c** exist as triarylborane adducts could be seen immediately from their ^{1}H-NMR spectra which revealed, in addition to a singlet at $\delta = 1.3$ for the *tert*-butyl group at C-2, typical signals in the aromatic region ($\delta = 6.80-7.85$) and the correct integration ratios between aliphatic and aromatic protons. The complexed ring phosphorus atoms of **20b** and **c** gave ^{31}P-NMR signals at $\delta = -171.2$ to -173.2 which were thus shifted by about 20 ppm to low-field in comparison to that of **19b** ($\delta = -189.5$). This is in agreement with the general trend that an increase in the coordination of a phosphirene phosphorus atom is accompanied by a shift of the phosphorus signal to lower field[41]. The signals of the ring carbon atoms and for the ipso-carbon atom of the 1-aryl substituent were characteristic for **19b** and **20b** and **c**. All three signals appeared as doublets with $^1J_{C,P}$ coupling constants of 27.9–66.4 Hz in the olefinic region of the ^{13}C-NMR spectra. As already mentioned for the 1*H*-phosphirenes, **15f–p**, the coupling to the exocyclic carbon atoms were in this case again up to 25 Hz larger than the $^1J_{C,P}$ couplings. In comparison with the complexed derivatives, the corresponding couplings of the free 1*H*-phosphirenes were, on average, 10 Hz larger. This also follows the general trend, that increases in coordination at phosphorus atoms in a three-membered ring are accompanied by, in some cases drastic, reductions in size of the $^1J_{P,C}$ couplings[41].

When sodium triethylborate (**18a**) was allowed to react with the 1*H*-phosphirene, **5a**, 1-ethyl-1*H*-phosphirene (**19a**, ≡**15f**) was isolated in 45% yield. The spectroscopic data for this product were in complete agreement with those of the compound already prepared by a different route. Alkali metal triethylborates are powerful ethylating agents[42] that undergo transmetallation reactions with metal halides[43]. Hence, the successful reaction with **5a** was not surprising. However, we cannot explain at present why the triethylborane liberated in the reaction did not form an adduct with **19a**. The stability of Lewis base adducts depends on the nature of the employed borane; tribromoborane forms the most stable adducts and trialkoxyboranes the least stable[44]. However, the differences between triaryl- and trialkylboranes are only slight so that other effects such as, for example, steric factors, must provide the reason for the nonformation of an adduct. On the basis of the above observations, it is understandable that the reactions of **5** with the alkoxyborates, **18d–g**, stopped at the stage of the 1-alkoxy-1*H*-phosphirenes, **19d–g**, and that no adducts corresponding to **20** [(R^2)$_3$ = OR′] were observed. The yields decreased with increasing size of the alkoxy group (77% → 33%). The 1*H*-phosphirene, **19d**, is identical in all respects to the previously prepared compound, **15a**, and the spectroscopic data for **19e–f** differed only minimally from those of **15a**, so that a detailed discussion is not necessary. One feature worthy of note, however, is that the methyl groups of the isopropyl substituent in **19f** are diastereotopic on account of the chiral phosphorus atom, and gave rise to signals with differing chemical shifts in the ^{1}H-NMR and ^{13}C-NMR spectra (see Experimetnal Section). The mass spectrum of **19f** contained, in addition to the molecular ion peak (71%), a fragment ion at *m/z* = 189 (21%) which was assigned to a phosphirenylium cation. Thus, the generation of the cation **10**[15] at low temperature in liquid SO_2 has also been demonstrated in a gas-phase reaction.

The ^{31}P-NMR spectrum of the 1*H*-phosphirene, **19g**, which bears two alkoxy substituents, revealed, in comparison to all other currently known 1*H*-phosphirenes, the most downfield-shifted signal (**19d**: $\delta = -77.1$; **19g**: $\delta = -40.0$). The polarization of the phosphirene double bond was easily recognized by the widely differing ^{13}C-NMR chemical shift values for C-2 ($\delta = 120.6$) and C-3 ($\delta = 153.9$), demonstrating the enol ether nature of this bond.

Reactions of 5 with Trimethylsilyl Nucleophiles, 21a and b

Nucleophilic substitution reactions at 1-halo-1*H*-phosphirenes are also possible by condensation with trimethylsilyl nucleophiles[24,45]. It was found advantageous to employ the trimethylsilyl nucleophiles **21a** and **b** in a large excess (i.e., practically as the solvent) in reactions with **5**. In this way, the 1-cyano- and the surprisingly stable[46] 1-azido-1*H*-phosphirenes, **22a**−**d**, were obtained in analytically pure form and in up to quantitative yields.



5 **22**

21	a	b
R2	CN	N3

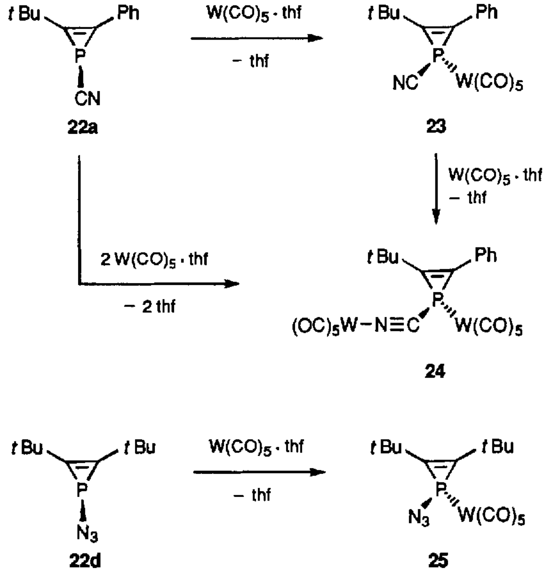
22	a	b	c	d
R1	Ph	OEt	Ph	*t*Bu
R2	CN	CN	N3	N3

The C≡N valency vibrations of **22a** and **b** (2145 and 2150 cm^{-1}, respectively) and the azide valency vibrations of **22c** and **d** (2090 and 2100 cm^{-1}, respectively) can be easily recognized in the IR spectra of **22a**−**d**. These bands were shifted by about 20−70°C cm^{-1} to lower wavenumber in comparison to those of other trivalent cyanophosphanes[47,48] and other azides[49]; this is indicative of a weakening of the triple bond character in the functional group.

In the ^{31}P-NMR spectra of **22a** and **b** the phosphorus signals appeared at very high-field ($\delta = -232.4$ and -182.0) and were comparable to those of the 1-alkynyl derivative, **15k** ($\delta = -228.0$). The probable reason for this is the anisotropic effect of the triple bond, which effects a shielding of the atoms in the α position[50]. The signal of **22b** was shifted by 50 ppm to lower field in comparison with that of **22a**. This reflected the influence of the ethoxy group at the phosphirene double bond and is characteristic for this particular structural element. The ^{31}P-NMR signals for the 1-azido-1*H*-phosphirenes **22c** and **d** appeared at $\delta = -106.7$ and -106.3, respectively. These values were similar to those of the 1-amino-substituted 1*H*-phosphirenes, **15c**−**e** ($\delta = -127.2$ to -113.9)[13]. The ^{13}C-NMR data for **22a**−**d** are comparable in all respects with those of the 1*H*-phosphirenes, **15a**−**t**, and, with the exception of the large exocyclic $^{1}J_{C,P}$ coupling to the cyanide carbon atoms in **22a** and **b** (181.0 and 193.5 Hz, respectively), do not present any features worthy of particular mention. In the ^{1}H-NMR spectrum of **22b**, the methylene protons of the ethoxy group appear as the AB part of an ABX spin system as a consequence of the diastereotopy (see also Experimental Section).

Like **5a**, the substituent bonded to phosphorus in the 1-cyano-1*H*-phosphirene **22a** can also undergo nucleophilic substitution. As an example, substitution with methyllithium (**14e**) was investigated and found to produce the already known 1-methyl-1*H*-phosphirene, **15f**[24], in a smooth reaction.

When the 1*H*-phosphirenes, **22a** and **22d**, were allowed to react with pentacarbonyltungsten · THF, complexation occurred and the crystalline η^1-tungsten complexes, **23** and **25**, were obtained in yields of 13 and 11%. Complexation of **22a** furnished, in addition to **23**, the complex, **24**, containing two pentacarbonyltungsten fragments. In addition to the end-on coordination of the fragment at phosphorus, this complex contains a second fragment in a similar end-on coordination at the nitrogen atom of the cyanide group. Complex **24** can also be prepared from **23** by reaction with pentacarbonyltungsten · THF.



The structures of the novel complexes **23**−**25** were unequivocally determined from their analytical and spectroscopic data. The spectroscopic data for **23** agree very well with those of a previously known complex with an analogous structure except for the replacement of the *tert*-butyl substituent at C-2 by a phenyl group[51]. The valency vibrations of the cyano, azido, and carbonyl groups in the IR spectrum can be readily assigned. The fact that the value for the C≡N valency vibration hardly changes on transformation of **23** into **24** (**23**: 2167 cm^{-1}, **24**: 2149 cm^{-1}) can be taken as evidence for the frequently observed end-on coordination of the nitrile nitrogen atom[52,53]. The ^{31}P- and ^{13}C-NMR signals for the atoms of the three-membered heterocyclic ring are, as expected, paramagnetically shifted in comparison to those of the uncomplexed 1*H*-phosphirenes (see also the discussion of the iron tetracarbonyl complex **16** and the references cited there). Furthermore, the characteristic $^{1}J_{P,W}$ coupling constants of 312–317 Hz were observed in the ^{31}P-NMR spectra, confirming the end-on coordination of the pentacarbonyltungsten fragment to the phosphorus atom.

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Table 1. Yields and selected spectroscopic data for **15a–t**

15	Yield [%]	^{31}P-NMR[a]	^{13}C-NMR[a, b] C-2 (d, $^{1}J_{PC}$)	^{13}C-NMR[a, b] C-3 (d, $^{1}J_{PC}$)	^{13}C-NMR[a, b] C-*exo* (d, $^{1}J_{PC}$)
a	71	–71.1	155.6 (69.5)	138.6 (56.9)	–
b	55	–75.1	150.1 (60.6)	150.1 (60.6)	–
c	76	–115.9	151.9 (59.3)	133.4 (47.6)	–
d	75	–127.2	149.5 (58.6)	130.8 (48.2)	–
e	72	–113.9	155.2 (66.2)	132.0 (56.5)	–
f	53	–194.0	138.3 (47.8)	119.4 (41.9)	17.7 (54.3)
g	77	–175.2	138.1 (49.2)	119.7 (43.8)	25.3 (52.1)
h	67	–145.2	140.0 (50.3)	121.6 (41.8)	29.8 (32.9)
i	36	–177.2	139.9 (50.4)	120.3 (43.7)	139.0 (80.8)
j	86	–186.6	136.2 (47.3)	117.7 (40.4)	149.5 (65.5)
k[c]	35	–228.0	135.5 (49.1)	116.2 (43.1)	83.8 (110.2)
l	49	–183.2	140.3 (51.8)	121.7 (45.8)	22.7 (69.0)
m	90	–159.6	142.0 (52.0)	125.0 (51.0)	21.8 (88.7)
n	90	–122.7	147.6 (65.5)	129.2 (51.1)	12.4 (112.7)
o[d]	100[e]	–178.8	138.4 (56.2)	120.6 (48.9)	30.3 (63.5)
p[d]	100[e]	–183.8	132.2 (53.4)	132.2 (53.4)	31.0 (54.7)
q	90	–205.5	130.9 (56.2)	111.5 (45.2)	–
r	90	–203.1	122.0 (51.8)	122.0 (51.8)	–
s	90	–139.6	85.8 (33.7)	133.3 (55.4)	–
t	80	–189.0	132.9 (57.9)	113.2 (48.9)	–

[a] δ in ppm. – [b] *J* in Hz. – [c] IR (film): $\tilde{\nu}$ = 2160 cm^{-1} (C≡C). – [d] IR (film): $\tilde{\nu}$ = 2040 cm^{-1} (C=N$_2$). – [e] Yield of the crude product.

Experimental Section

General: All reactions were carried out under argon (purity >99.998%) in previously baked-out and evacuated apparatus. – Melting points (uncorrected, sealed capillary tubes): Mettler FP 61 (heating rate 3°C/min). – Microanalyses: Perkin-Elmer-Analyser EA 240 and 2400 CHN. – Bulb-to-bulb distillations: Büchi GKR 50 apparatus (temperatures given refer to the heating mantle). – MS: Finnigan MAT 90. – IR: Perkin-Elmer 710 B, Perkin-Elmer IR 394. – ^{1}H NMR: Varian EM 360, Varian EM 390, Bruker WP 200, and Bruker AM 400 spectrometers at 60, 90, 200, and 400 MHz, respectively. – ^{13}C NMR and ^{31}P NMR: Bruker WP 200 and Bruker AM 400 spectrometers at 50.32, 100.64 MHz (^{13}C), 80.8 and 161.6 MHz (^{31}P), respectively. – Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (δ) relative to tetramethylsilane as the internal standard; the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. – The 1-chloro-1*H*-phosphirenes, **5**, were prepared as described recently[14]. Trimethylsilylmethylmagnesium chloride (**14k**)[54], bis(trimethylsilyl)methyllithium (**14l**)[54], tris(trimethylsilyl)methyllithium (**14m**)[54], tris(trimethylsilyl)silyllithium (**14o**)[55], tris(trimethylsilyl)germyllithium (**14p**)[56], and sodium tetrakis(4-chlorophenyl)borate (**18c**)[57] were prepared according to published procedures. Compounds **14j** and **n** were prepared by lithiation of 3,3-dimethylbut-1-yne[58] (→**14j**) or diazotrimethylsilylmethane[59] (→**14n**) with *n*-butyllithium. All other starting materials were purchased from commercial suppliers.

1H-Phosphirenes **15a–t**

General Procedure for the Synthesis of P-Substituted 1H-Phosphirenes **15a–t**: A solution of **5** in a suitable solvent was added dropwise at –78°C to the organolithium, or at 0°C to the Grignard reagent, **14a–p**, in diethyl ether or THF solution. The mixture was stirred for 10–60 min at the temperature of the addition and then allowed to warm slowly to room temperature. The mixture was then treated using one of two processes. In method A, the lithium or Grignard salts were removed using a centrifuge and the solvents evaporated in vacuum; in method B, the solvents were evaporated first, the residue taken up in hexane, and the mixture filtered or centrifuged, and then concentrated in vacuum. The crude oils were purified by bulb-to-bulb distillation and/or flash chromatography and the 1*H*-phosphirenes **15** were obtained as colorless or pale yellow liquids which were analytically pure but, in some cases, slowly decomposed at room temperature.

2-tert-Butyl-1-methoxy-3-phenyl-1H-phosphirene (**15a**): From **5a** (0.56 g, 2.49 mmol) in pentane (10 ml) and **14a** (0.10 g, 2.63 mmol) in diethyl ether (20 ml). Bulb-to-bulb distillation of the crude oil (method A) at 130°C/10^{-2} mbar yielded **15a** (0.39 g, 71%) as a colorless liquid. – ^{1}H NMR (CDCl$_3$): δ = 1.44 (s, 9H, *t*Bu), 3.03 (d, $^{3}J_{H,P}$ = 12.2 Hz, OMe), 7.61 (m, 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 29.7 [s, [C(*C*H$_3$)$_3$], 34.0 [d, $^{2}J_{C,P}$ = 6.5 Hz, *C*(CH$_3$)$_3$], 50.1 (s, OCH$_3$), 128.4 (d, $^{2}J_{C,P}$ = 6.7 Hz, *i*-C), 129.0, 129.3, 130.7 (each s, *o*-, *m*-, *p*-C), 138.6 (d, $^{1}J_{C,P}$ = 56.9 HZ, C-3), 155.6 (d, $^{1}J_{C,P}$ = 69.5 Hz, C-2). – ^{31}P NMR (CDCl$_3$): δ = –77.1. – C$_{13}$H$_{17}$PO (220.2): calcd. C 70.89, H 7.78; found C 70.5, H 7.62. Compound **15a** can also be obtained by reaction of **5a** with lithium tetramethoxyborate (**18d**) or with sodium tetrahydroborate in methanol/diethyl ether[24].

2,3-Di-tert-butyl-1-methoxy-1H-phosphirene (**15b**): From **5b** (0.15 g, 0.73 mmol) in pentane (3 ml) and sodium methoxide (0.04 g, 0.74 mmol) (instead of **14a**) in diethyl ether (3 ml). Bulb-to-bulb distillation of the crude oil (method A) at 120°C/10^{-2} mbar yielded **15b** (0.08 g, 55%) as a colorless liquid. – ^{1}H NMR (CDCl$_3$): δ = 1.29 (s, 18H, *t*Bu), 2.99 (d, $^{2}J_{H,P}$ = 10.3 Hz, 3H, OMe). – ^{13}C NMR (CDCl$_3$): δ = 30.1 [s, C(*C*H$_3$)$_3$], 32.7 [d, $^{2}J_{C,P}$ = 7.0 Hz, *C*(CH$_3$)$_3$], 49.6 (s, OCH$_3$), 150.1 (d, $^{1}J_{C,P}$ = 60.6 Hz, C-2, C-3). –

^{31}P NMR ($CDCl_3$): δ = −75.1. – MS (70 eV); *m/z* (%): 200 (3) [M$^+$], 169 (100) [M$^+$ – OCH_3].

2-tert-Butyl-1-(N,N-diethylamino)-3-phenyl-1H-phosphirene (**15c**): From **5a** (0.28 g, 1.25 mmol) in pentane (10 ml) and **14b** (0.10 g, 1.26 mmol) in diethyl ether (10 ml). Bulb-to-bulb distillation of the crude oil (method A) at 150°C/10^{-2} mbar yielded **15c** (0.25 g, 76%) as a colorless liquid. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, $^{3}J_{H,H}$ = 7.0 Hz, 6H, NCH_2CH_3), 1.36 (s, 9H, *t*Bu), 2.73 (m, 4H, NCH_2CH_3), 7.27, 7.38, 7.60 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.3 (s, NCH_2CH_3), 29.5 [s, $C(CH_3)_3$], 33.6 [d, $^{2}J_{C,P}$ = 5.5 Hz, $C(CH_3)_3$], 38.5 (d, $^{2}J_{C,P}$ = 13.8 Hz, NCH_2CH_3), 128.0, 128.4, 129.8 (each s, *o*-, *m*-, *p*-C), 131.5 (d, $^{2}J_{C,P}$ = 6.7 Hz, *i*-C), 133.4 (d, $^{1}J_{C,P}$ = 47.6 Hz, C-3), 151.9 (d, $^{1}J_{C,P}$ = 59.3 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −115.9. – MS (70 eV); *m/z* (%): 261 (38) [M$^+$], 246 (3) [M$^+$ – CH_3], 204 (17) [M$^+$ – C_4H_9], 189 (23) [M$_+$ – $N(C_2H_5)_2$], 158 (7), 143 (28), 128 (17), 103 (100), 74 (72), 72 (16). – $C_{16}H_{24}NP$ (261.4): calcd. C 73.53, H 9.26, N 5.36; found C 73.5, H 9.2, N 5.2.

2-tert-Butyl-1-(N,N-disopropylamino)-3-phenyl-1H-phosphirene (**15d**): From **5a** (0.34 g, 1.51 mmol) in pentane (10 ml) and **14c** (0.16 g, 1.51 mmol) in diethyl ether (10 ml). Bulb-to-bulb distillation of the crude oil (method A) at 130°C/10^{-2} mbar yielded **15d** (0.32 g, 75%) as a colorless liquid. – ^{1}H NMR ($CDCl_3$): δ = 1.13 (d, $^{3}J_{H,H}$ = 7.5 Hz, 12H, $NCHCH_3$), 1.38 (s, 9H, *t*Bu), 3.15 (m, 2H, $NCHCH_3$), 7.55 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 23.9 (d, $^{3}J_{C,P}$ = 7.3 Hz, $NCHCH_3$), 24.0 (d, $^{3}J_{C,P}$ = 6.2 Hz, $NCHCH_3$), 29.9 [s, $C(CH_3)_3$], 34.1 [d, $^{2}J_{C,P}$ = 6.4 Hz, $C(CH_3)_3$], 43.2 (d, $^{2}J_{C,P}$ = 5.7 Hz, $NCHCH_3$), 128.3, 128.9, 130.6 (each s, *o*-, *m*-, *p*-C), 130.8 (d, $^{1}J_{C,P}$ = 48.2 Hz, C-3), 132 (d, $^{2}J_{C,P}$ = 7.1 Hz, *i*-C), 149.5 (d, $^{1}J_{C,P}$ = 58.6 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −127.2. – $C_{18}H_{28}NP$ (289.4): calcd. C 74.71, H 9.75, N 4.84; found C 74.1, H 9.54, N 4.6.

2-tert-Butyl-1-[N,N-bis(trimethylsilyl)amino]-3-phenyl-1H-phosphirene (**15e**): From **5a** (0.36 g, 1.60 mmol) in pentane (10 ml) and **14d** (0.27 g, 1.60 mmol) in diethyl ether (10 ml). Bulb-to-bulb distillation of the crude oil (method A) at 200°C/10^{-2} mbar yielded **15e** (0.40 g, 72%) as a colorless liquid. – ^{1}H NMR ($CDCl_3$): δ = 0.14 (d, $^{4}J_{H,P}$ = 1.3 Hz, 18H, $NSiCH_3$), 1.36 (s, 9H, *t*Bu), 7.30, 7.40, 7.64 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 4.1 (d, $^{3}J_{C,P}$ = 6.7 Hz, $NSiCH_3$), 29.5 [s, $C(CH_3)_3$], 34.5 [d, $^{2}J_{C,P}$ = 8.0 Hz, $C(CH_3)_3$], 128.2, 128.3, 130.1 (each s, *o*-, *m*-, *p*-C), 131.0 (d, $^{2}J_{C,P}$ = 8.8 Hz, *i*-C), 132.0 (d, $^{1}J_{C,P}$ = 56.5 Hz, C-3), 155.2 (d, $^{1}J_{C,P}$ = 66.2 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −113.9. – MS (70 eV); *m/z* (%): 349 (35) [M$^+$], 334 (27) [M$^+$ – Me], 192 (100), 176 (92), 158 (65), 143 (94), 128 (80), 103 (46), 77 (17), 73 (97), 45 (12).

2-tert-Butyl-1-methyl-3-phenyl-1H-phosphirene (**15f**): From **5a** (0.25 g, 1.11 mmol) in hexane (5 ml) and **14e** (0.7 ml, 1.12 mol; 1.6 M solution in diethyl ether). Bulb-to-bulb distillation of the crude oil after evaporation of the solvents under vacuum at 180°C/10^{-1} mbar yielded **15f** (0.12 g, 53%) as a colorless liquid. – ^{1}H NMR ($CDCl_3$): δ = 0.70 (d, $^{2}J_{H,P}$ = 6.1 Hz, PCH_3), 1.38 (s, 9H, *t*Bu), 7.35, 7.65 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 17.7 (d, $^{1}J_{C,P}$ = 54.3 Hz, PCH_3), 29.5 [s, $C(CH_3)_3$], 33.9 [d, $^{2}J_{C,P}$ = 7.0 Hz, $C(CH_3)_3$], 119.4 (d, $^{1}J_{C,P}$ = 41.9 Hz, C-3), 128.1, 128.5, 130.4 (each s, *o*-, *m*-, *p*-C), 129.8 (d, $^{2}J_{C,P}$ = 8.5 Hz, *i*-C), 138.3 (d, $^{1}J_{C,P}$ = 47.8 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −194.0. – MS (70 eV); *m/z* (%): 204 (46) [M$^+$], 189 (76) [M$^+$ – CH_3], 147 (539) [M$^+$ – C_4H_9], 143 (56), 133 (100), 128 (53), 77 (26), 57 (48). Product **15f** was also obtained by reaction of 2-*tert*-butyl-1-cyano-3-phenyl-1*H*-phosphirene (**22a**) with **14e**; yield: 46%[24].

2-tert-Butyl-1-ethyl-3-phenyl-1H-phosphirene [**15g** (≡**19a**)]: From **5a** (0.2 g, 1.07 mmol) in diethyl ether (3 ml) and **14f** (0.91 ml, 1.07 mmol, 1.17 M solution in diethyl ether). Bulb-to-bulb distillation of the crude oil (method B) at 200°C/10^{-1} mbar yielded **15g** (0.18 g, 77%) as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 2962, 2913, 1757, 1590, 1485, 1474, 1458, 1444, 1360, 1187, 1171, 1072, 1028, 761, 691 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.98 (m, 3H, CH_2CH_3), 1.10 (m, 2H, CH_2CH_3), 1.35 (s, 9H, *t*Bu), 7.16, 7.28, 7.78 (each m, 5H aromatic H). – ^{13}C NMR (C_6D_6): δ = 10.7 (d, $^{2}J_{C,P}$ = 9.2 Hz, CH_2CH_3), 25.3 (d, $^{1}J_{C,P}$ = 52.1 Hz, CH_2CH_3), 28.3 [s, $C(CH_3)_3$], 33.7 [d, $^{2}J_{C,P}$ = 8.2 Hz, $C(CH_3)_3$], 119.7 (d, $^{1}J_{C,P}$ = 43.8 Hz, C-3), 128.4, 128.8, 131.0 (each s, *o*-, *m*-, *p*-C), 130.9 (d, $^{2}J_{C,P}$ = 8.2 Hz, *i*-C), 138.1 (d, $^{1}J_{C,P}$ = 49.2 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −175.2. – $C_{14}H_{19}P$ (218.3): calcd. C 77.04, H 8.77; found C 76.6, H 8.7. Compound **15g** (≡**19a**) can also be obtained by reaction of **5a** with sodium tetraethylborate (**18a**).

1,2-Di-tert-butyl-3-phenyl-1H-phosphirene (**15h**): From **5a** (0.56 g, 2.49 mmol) in pentane (10 ml) and **14g** (0.16 g, 2.49 mmol) in diethyl ether (20 ml). Bulb-to-bulb distillation of the crude oil (method A) at 150°C/10^{-2} mbar yielded **15h** (0.41 g, 67%) as a colorless liquid. – ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, $^{3}J_{H,P}$ = 12.6 Hz, 9H, *t*Bu-1), 1.39 (s, 9H, *t*Bu-2), 7.49 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.4 [d, $^{2}J_{C,P}$ = 15.7 Hz, $PC(CH_3)_3$], 29.8 [d, $^{1}J_{C,P}$ = 32.9 Hz, $PC(CH_3)_3$], 29.9 [s, $C(CH_3)_3$], 33.0 [d, $^{2}J_{C,P}$ = 9.2 Hz, $C(CH_3)_3$], 121.6 (d, $^{1}J_{C,P}$ = 41.8 Hz, C-3), 128.2, 128.6, 130.7 (each s, *o*-, *m*-, *p*-C), 130.5 (d, $^{2}J_{C,P}$ = 10.1 Hz, *i*-C), 140.0 (d, $^{1}J_{C,P}$ = 50.3 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −145.2. – $C_{16}H_{23}P$ (246.3): calcd. C 78.01, H 9.41; found C 77.4, H 9.15.

2-tert-Butyl-1-mesityl-3-phenyl-1H-phosphirene (**15i**): From **5a** (0.30 g, 1.34 mmol) in diethyl ether (3 ml) and **14h** (1.60 ml, 1.34 mmol, 0.84 M solution in diethyl ether). The crude product (method B) was purified by flash chromatography on aluminum oxide (3.0 g) with 150 ml hexane/diethyl ether (20:1) instead of bulb-to-bulb distillation. Product **15i** (0.15 g, 36%) was obtained as colorless crystals from dichloromethane (−78°C) which decomposed slowly at room temperature. – ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 9H, *t*Bu), 2.17 (s, 3H, *p*-CH_3-Mes), 2.41 (s, 6H, *o*-, *o'*-CH_3-Mes), 6.67 (s, 2H, *m*, *m'*-H-Mes), 7.32, 7.42, 7.67 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.9 (s, *p*-CH_3-Mes), 22.7 (d, $^{3}J_{C,P}$ = 13.2 Hz, *o*-, *o'*-CH_3-Mes), 29.2 [s, $C(CH_3)_3$], 34.2 [d, $^{2}J_{C,P}$ = 8.5 Hz, $C(CH_3)_3$], 120.3 (d, $^{1}J_{C,P}$ = 43.7 Hz, C-3), 128.1, 128.4, 128.8 (each s, *o*-, *m*-, *p*-C), 130.1 (s, *m*-, *m'*-C-Mes), 130.5 (d, $^{2}J_{C,P}$ = 8.1 Hz, *i*-C), 136.7 (s, *p*-C-Mes), 139.0 (d, $^{1}J_{C,P}$ = 80.8 Hz, *i*-C-Mes), 139.9 (d, $^{1}J_{C,P}$ = 50.4 Hz, C-2), 141.4 (d, $^{2}J_{C,P}$ = 11.4 Hz, *o*-C-Mes). – ^{31}P NMR ($CDCl_3$): δ = −177.2.

2-tert-Butyl-1-ethenyl-3-phenyl-1H-phosphirene (**15j**): From **5a** (0.24 g, 1.97 mmol) in toluene (3 ml) and **14i** (2.14 ml, 1.07 mmol, 0.5 M solution in THF). Bulb-to-bulb distillation of the crude oil (method B, pentane instead of hexane) at 200°C/10^{-2} mbar and subsequent flash chromatography on silica gel (3 g, 15–40 µm) with hexane yielded **15j** (0.20 g, 86%) as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3045, 2960, 1768, 1599, 1582, 1485, 1474, 1458, 1443, 1384, 1360, 1259, 1185, 1170, 1070, 1025, 983, 928, 760, 690, 677 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 1.23 (s, 9H, *t*Bu), 5.45 (ddd, $^{2}J_{AC}$ = 1.9 Hz, $^{3}J_{cisBC}$ = 11.6 Hz, $^{3}J_{H,P}$ = 32.0 Hz, 1H, $CH_B{=}CH_AH_C$), 5.83 (ddd, $^{2}J_{H,P}$ = 3.6 Hz, $^{3}J_{cisBC}$ = 11.6 Hz, $^{3}J_{transAB}$ = 18.9 Hz, 1H, $CH_B{=}CH_AH_C$), 5.89 (ddd $^{2}J_{AC}$ = 1.9 Hz, $^{3}J_{H,P}$ = 15.0 Hz, $^{3}J_{transAB}$ = 18.9 Hz, 1H, $CH_B{=}CH_AH_C$), 7.09, 7.14, 7.65 (each m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 29.4 [s, $C(CH_3)_3$], 33.9 [d, $^{2}J_{C,P}$ = 7.8 Hz, $C(CH_3)_3$], 117.7 (d, $^{1}J_{C,P}$ = 40.4 Hz, C-3), 126.5 (d, $^{2}J_{C,P}$ = 29.8 Hz, $CH_B{=}CH_AH_C$), 128.6, 128.9, 130.9 (each s, *o*-, *m*-, *p*-C), 130.0 (d, $^{2}J_{C,P}$ = 7.2 Hz, *i*-C), 136.2 (d, ${}^1J_{C,P}$ = 47.3 Hz, C-2), 149.5 (d, ${}^1J_{C,P}$ = 65.5 Hz, $CH_B{=}CH_AH_C$). – ^{31}P NMR ($CDCl_3$): δ = −186.6. – $C_{14}H_{17}P$ (216.26): calcd. C 77.75, H 7.92; found C 78.30, H 7.94.

2-tert-Butyl-1-(3,3-dimethyl-but-1-ynyl)-3-phenyl-1H-phosphirene (**15k**): From **5a** (0.56 g, 2.5 mmol) in pentane (10 ml) and **14j** [prepared from 3,3-dimethylbut-1-yne (0.21 g, 2.5 mmol) and 2-methylpropyllithium (0.16 g, 2.5 mmol)]. Bulb-to-bulb distillation of the crude oil (method A) at 120°C/10^{-2} mbar yielded **15k** (0.29 g, 35%) as a colorless liquid. – IR (film): ṽ = 2160 cm^{-1} (C≡C). – ^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 9H, *t*Bu-C≡C), 1.42 (s, 9H, *t*Bu), 7.6 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 27.9 [s, C≡C-$C(CH_3)_3$], 29.4, 30.9 [each s, $C(CH_3)_3$], 34.3 [d, ${}^2J_{C,P}$ = 6.9 Hz, $C(CH_3)_3$], 83.8 (d, ${}^1J_{C,P}$ = 110.2 Hz, P−C≡C), 96.9 (d, ${}^2J_{C,P}$ = 20.6 Hz, P−C≡C), 116.2 (d, ${}^1J_{C,P}$ = 43.1 Hz, C-3), 128.9, 128.5, 130.9 (each s, *o*-, *m*-, *p*-C), 133.5 (d, ${}^1J_{C,P}$ = 49.1 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −228.0.

2-tert-Butyl-3-phenyl-1-trimethylsilylmethyl-1H-phosphirene (**15l**): From **5a** (0.67 g, 3.0 mmol) in diethyl ether (15 ml) and **14k** (0.49 g, 3.3 mmol) in diethyl ether. In contrast to the general procedure, the Grignard solution was added to the solution of **5a**. Bulb-to-bulb distillation of the crude oil (method B) at 125°C/10^{-2} mbar yielded **15l** (0.49 g, 60%) as a colorless liquid. – IR (film): ṽ = 3050, 2950, 1750, 1590, 1460, 1430, 1350, 1240, 1050, 850, 830, 760, 690 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.30 [s, 9H, $Si(CH_3)_3$], 0.60 (m, 2H, CH_2), 1.50 (s, 9H, *t*Bu), 7.3–8.0 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 0.10 [s, $Si(CH_3)_3$], 22.7 [d, ${}^1J_{C,P}$ = 69.0 Hz, $CH_2Si(CH_3)_3$], 29.75 [s, $C(CH_3)_3$], 34.1 [d, ${}^2J_{C,P}$ = 7.4 Hz, $C(CH_3)_3$], 121.7 (d, ${}^1J_{C,P}$ = 45.8 Hz, C-3), 128.4, 128.8, 130.8, 131.9 (each s, *o*-, *m*-, *p*-, *i*-C), 140.3 (d, ${}^2J_{C,P}$ = 51.8 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −183.2. – MS (70 eV); *m*/*z* (%): 276 (29) [M$^+$], 261 (6) [M$^+$ − CH_3], 189 (100), 158 (22), 143 (739, 73 (32).

1-Bis(trimethylsilylmethyl)-2-tert-butyl-3-phenyl-1H-phosphirene (**15m**): From **5a** (0.48 g, 2.0 mmol) in diethyl ether (10 ml) and **14l** [prepared from bis(trimethylsilyl)bromomethane (0.42 g, 2.0 mmol) and *n*-butyllithium (1.31 ml, 2.1 mmol, 1.6 M solution in hexane)] in diethyl ether (10 ml). Bulb-to-bulb distillation of the crude oil (method B) at 150°C/10^{-3} mbar yielded **15m** (0.63 g, 90%) as a pale yellow liquid. – IR (film): ṽ = 2950, 1590, 1430, 1350, 1250, 1000, 840, 750, 690 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.10 [d, ${}^2J_{H,P}$ = 2.0 Hz, $CHSi(CH_3)_3$], 0.30 [s, 9H, $Si(CH_3)_3$], 0.60 (s, 9H, *t*Bu), 7.3–8.0 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 1.86 [d, ${}^3J_{C,P}$ = 7.0 Hz, $Si(CH_3)_3$], 2.1 [s, $Si(CH_3)_3$], 21.8 [d, ${}^1J_{C,P}$ = 88.7 Hz, $CHSi(CH_3)_3$], 29.6 [s, $C(CH_3)_3$], 43.5 [d, ${}^2J_{C,P}$ = 8.2 Hz, $C(CH_3)_3$], 125.0 (d, ${}^1J_{C,P}$ = 51.0 Hz, C-3), 128.2, 128.6, 128.9 (each s, *o*-, *m*-, *p*-C), 131.6 (d, ${}^2J_{C,P}$ = 7.6 Hz, *i*-C), 142.0 (d, ${}^1J_{C,P}$ = 52.0 Hz, C-2). – ^{31}P NMR ($CDCl_3$): δ = −159.6. – MS (70 eV); *m*/*z* (%): 348 (7) [M$^+$], 333 (2) [M$^+$ − CH_3], 189 (23), 185 (32), 143 (100), 77 (9), 73 (43).

2-tert-Butyl-3-phenyl-1-tris(trimethylsilyl)methyl-1H-phosphirene (**15n**): From **5a** (0.45 g, 2.0 mmol) in diethyl ether and **14m** [prepared from bromotris(trimethylsilyl)methane (0.62 g, 2.0 mmol) and *n*-butyllithium (1.31 ml, 2.1 mmol, 1.6 M soluton in hexane)] in diethyl ether (10 ml). Bulb-to-bulb distillation of the crude oil (method B) at 170°C/10^{-3} mbar yielded **15n** (0.80 g, 90%) as a pale yellow liquid. – IR (film): ṽ = 2950, 1590, 1350, 1250, 1060, 840, 760, 690 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.60 [s, 27H, $Si(CH_3)_3$], 1.60 (s, 9H, *t*Bu), 7.3–8.0 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 4.4 [d, ${}^3J_{C,P}$ = 6.2 Hz, $Si(CH_3)_3$], 12.4 [d, ${}^1J_{C,P}$ = 112.7 Hz, $CSi(CH_3)_3$], 30.4 [s, $C(CH_3)_3$], 35.7 [d, ${}^2J_{C,P}$ = 8.4 Hz, $C(CH_3)_3$], 128.3, 128.6, 129.7 (each s, *o*-, *m*-, *p*-C), 129.2 (d, ${}^1J_{C,P}$ = 51.1 Hz, C-3), 131.0 (d, ${}^2J_{C,P}$ = 9.3 Hz, *i*-C), 147.6 (d, ${}^1J_{C,P}$ = 65.5 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −122.7.

2-tert-Butyl-1-(diazo-trimethylsilylmethyl)-3-phenyl-1H-phosphirene (**15o**): From **5a** (0.56 g, 2.5 mmol) in pentane (10 ml) and **14n** (0.30 g, 2.5 mmol) in diethyl ether (20 ml). The yellow crude **15o** (0.80 g, 100%) (method A) could not be further purified without decomposition. – IR (film): ṽ = 2040 cm^{-1} (C=N$_2$). – ^{1}H NMR (C_6D_6): δ = 0.29 [s, 9H, $Si(CH_3)_3$], 1.39 (s, 9H, *t*Bu), 7.45 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = −1.1 [d, ${}^3J_{C,P}$ = 3 Hz, $Si(CH_3)_3$], 29.1 [s, $C(CH_3)_3$, 30.3 (d, ${}^1J_{C,P}$ = 63.5 Hz, C=N$_2$), 32.8 [d, ${}^2J_{C,P}$ = 6.5 Hz, $C(CH_3)_3$], 120.6 (d, ${}^1J_{C,P}$ = 48.9 Hz, C-3), 138.4 (d, ${}^1J_{C,P}$ = 56.2 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −178.8.

2,3-Di-tert-butyl-1-(diazo-trimethylsilylmethyl)-1H-phosphirene (**15p**): From **5b** (0.52 g, 2.50 mmol) in pentane (10 ml) and **14n** (0.30 g, 2.50 mmol) in diethyl ether (20 ml). The yellow crude **15p** (0.70 g, 100%) (method A) could not be further purified without decomposition. – IR (film): ṽ = 2040 cm^{-1} (C=N$_2$). – ^{1}H NMR (C_6D_6): δ = 0.27 [s, 9H, $Si(CH_3)_3$], 1.27 (s, 18H, *t*Bu). – ^{13}C NMR (C_6D_6): δ = −1.1 [d, ${}^3J_{C,P}$ = 3 Hz, $Si(CH_3)_3$], 29.7 [s, $C(CH_3)_3$], 31.0 (d, ${}^1J_{C,P}$ = 54.7 Hz, C=N$_2$), 31.7 [d, ${}^2J_{C,P}$ = 7.6 Hz, $C(CH_3)_3$], 132.2 (d, ${}^1J_{C,P}$ = 53.4 Hz, C-2, C-3). – ^{31}P NMR (C_6D_6): δ = −183.8.

2-tert-Butyl-3-phenyl-1-tris(trimethylsilyl)silyl-1H-phosphirene (**15q**): From **5a** (2.24 g, 10.0 mmol) in pentane and **14o** · 3 THF (4.7 g, 10.0 mmol) in pentane. Bulb-to-bulb distillation of the crude oil (method A) at 170°C/10^{-3} mbar yielded **15q** (3.9 g, 90%) as a colorless, waxy solid. – IR (film): ṽ = 2960, 2900, 1760, 1590, 1470, 1440, 1360, 1250, 1050, 850, 760, 700, 630 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.60 [s, 27H, $Si(CH_3)_3$], 1.60 (s, 9H, *t*Bu), 7.3–8.1 (m, 5H, armatic H). – ^{13}C NMR (C_6D_6): δ = 2.4 [s, $Si(CH_3)_3$], 29.8 [s, $C(CH_3)_3$], 33.9 [d, ${}^2J_{C,P}$ = 6.7 Hz, $C(CH_3)_3$], 111.5 (d, ${}^1J_{C,P}$ = 45.2 Hz, C-3), 128.5, 128.6, 131.3 (each s, *o*-, *m*-, *p*-C), 130.3 (d, ${}^2J_{C,P}$ = 6.3 Hz, *i*-C), 130.9 (d, ${}^1J_{C,P}$ = 56.2 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −205.5. – $C_{21}H_{41}PSi_4$ (436.9): calcd. C 57.73, H 9.46; found C 57.6, H 9.40.

2,3-Di-tert-butyl-1-tris(trimethylsilyl)silyl-1H-phosphirene (**15r**): From **5b** (0.40 g, 2.00 mmol) in pentane and **14o** · 3 THF (0.94 g, 2.00 mmol) in pentane. Bulb-to-bulb distillation of the crude oil (method A) at 160°C/10^{-3} mbar yielded **15r** (3.90 g, 90%) as colorless solid which melts at room temperature. – IR (film): ṽ = 2960, 2900, 1480, 1400, 1360, 1250, 1050, 850, 750, 700, 630 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.50 [s, 27H, $Si(CH_3)_3$], 1.40 (s, 9H, *t*Bu). – ^{13}C NMR (C_6D_6): δ = 2.7 [s, $Si(CH_3)_3$], 30.3 [s, $C(CH_3)_3$], 32.7 [d, ${}^2J_{C,P}$ = 8.2 Hz, $C(CH_3)_3$], 122.0 (d, ${}^1J_{C,P}$ = 51.8 Hz, C-2, C-3). – ^{31}P NMR (C_6D_6): δ = −203.1.

2-tert-Butyl-3-ethoxy-1-tris(trimethylsilyl)silyl-1H-phosphirene (**15s**): From **5c** (0.38 g, 2.00 mmol) in pentane and **14o** · 3 THF (0.94 g, 2.00 mmol) in pentane. Bulb-to-bulb distillation of the crude oil (method A) at 150°C/10^{-3} mbar yielded **15s** (0.72 g, 90%) as a pale yellow oil. – IR (film): ṽ = 2950, 2900, 1800, 1620, 1470, 1390, 1260, 1250, 1100, 1030, 840, 690, 630 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.50 [s, 27H, $Si(CH_3)_3$], 1.30 (t, ${}^3J_{H,H}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.40 (s, 9H, *t*Bu), 4.10 (q, ${}^3J_{H,H}$ = 7.0 Hz, 2H, OCH_2CH_3). – ^{13}C NMR (C_6D_6): δ = 2.3 [s, $Si(CH_3)_3$], 15.5 (s, OCH_2CH_3), 29.9 [s, $C(CH_3)_3$], 31.2 [d, ${}^2J_{C,P}$ = 5.7 Hz, $C(CH_3)_3$], 70.0 (s, OCH_2CH_3), 85.8 (d, ${}^1J_{C,P}$ = 33.7 Hz, C-2), 133.3 (d, ${}^1J_{C,P}$ = 55.4 Hz, C-3). – ^{31}P NMR ($CDCl_3$): δ = −139.6.

2-tert-Butyl-3-phenyl-1-tris(trimethylsilyl)germyl-1H-phosphirene (**15t**): From **5a** (0.90 g, 4.0 mmol) in pentane and **14p** · 3 THF (2.05 g, 4.0 mmol) in pentane (20 ml). Bulb-to-bulb distillation of the crude oil (method A) at 180°C/10^{-3} mbar yielded **15t** (1.54 g, 80%) as a yellow liquid. – ^{1}H NMR (C_6D_6): δ = 0.60 [s, 27H, $Si(CH_3)_3$], 1.60 (s, 9H, *t*Bu), 7.3–8.1 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 2.9 [s, $Si(CH_3)_3$], 29.6 [s, $C(CH_3)_3$], 33.9 [d, $^{2}J_{C,P}$ = 6.9 Hz, $C(CH_3)_3$], 113.2 (d, $^{1}J_{C,P}$ = 48.9 Hz, C-3), 128.5, 128.6, 131.4 (each s, *o*-, *m*-, *p*-C), 130.4 (d, $^{2}J_{C,P}$ = 6.6 Hz, *i*-C), 132.9 (d, $^{1}J_{C,P}$ = 57.9 Hz, C-2). – ^{31}P NMR (C_6D_6): δ = −189.0.

Reaction of **15q** *with Enneacarbonyldiiron [2-tert-Butyl-3-phenyl-1-tris(trimethylsilyl)silyl-1H-phosphirene]-tetracarbonyliron* (**16**): Compound **15q** (1.22 g, 2.80 mmol) was added at room temperature to a suspension of enneacarbonyldiiron (1.00 g, 2.80 mmol) in pentane (20 ml). Stirring was continued overnight while the iron carbonyl dissolved. Filtration of the solution, evaporation of the solvent in vacuum, and recrystallization twice from pentane at −78°C yielded **16** (0.85 g, 50%) as a brown solid. – IR (KBr): ṽ = 2950, 2900, 2020, 1960, 1930, 1430, 1360, 1250, 1060, 830 cm^{-1}. – ^{1}H NMR (C_6D_6): δ = 0.35 [s, 27H, $Si(CH_3)_3$], 1.60 (s, 9H, *t*Bu), 7.4–7.9 (m, 5H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 2.7 [s, $Si(CH_3)_3$], 30.1 [s, $C(CH_3)_3$], 35.2 [d, $^{2}J_{C,P}$ = 6.8 Hz, $C(CH_3)_3$], 127.8 (d, $^{2}J_{C,P}$ = 20.8 Hz, C-3), 128.7 (d, $^{2}J_{C,P}$ = 6.6 Hz, *i*-C), 129.0, 129.8, 130.2 (each s, *o*-, *m*-, *p*-C), 143.2 (d, $^{1}J_{C,P}$ = 27.4 Hz, C-2), 215.9 (d, $^{2}J_{C,P}$ = 17.6 Hz, C=O). – ^{31}P NMR (C_6D_6): δ = −141.0. – $C_{25}H_{41}FeO_4PSi_4$ (604.8): calcd. C 49.65, H 6.83; found C 49.1, H 6.78.

Reduction of **5a** *with Complex Hydrides*

2-tert-Butyl-3-phenyl-1H-phosphirene (**17**): 2-*tert*-Butyl-1-chloro-3-phenyl-1*H*-phosphirene (**5a**) (0.48 g, 2.14 mmol) was dissolved in diethyl ether (5 ml) and the solution was cooled at 0°C. A suspension of lithium aluminum hydride (0.04 g, 1.07 mmol) in diethyl ether (3ml) was added dropwise, the reaction mixture was stirred for 20 min at 0°C, then allowed to warm up to room temperature and stirred for a further 1 h. The solvent was removed in vacuum, the residue extracted with pentane, and the pentane solution was filtered over Celite. After removal of the pentane under vacuum, product **17** was obtained as a colorless liquid (0.31 g, 76%) which could not be purified without decomposition. Bulb-to-bulb distillation of crude **17** at 200°C/10^{-3} mbar yielded 3,3-dimethyl-1-phenyl-but-1-yne [*t*Bu–C≡C–Ph] (0.15 g, 58%). The alkyne was identified by comparison of its IR- and ^{1}H-NMR data with those of an authentic sample[60]. – IR (film): ṽ = 2275 cm^{-1} (P–H). – ^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 9H, *t*Bu), 1.54 (d, $^{1}J_{H,P}$ = 107.0 Hz, PH), 7.38, 7.67 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 29.2 [s, $C(CH_3)_3$], 33.0 [d, $^{2}J_{C,P}$ = 6.8 Hz, $C(CH_3)_3$], 108.1 (d, $^{1}J_{C,P}$ = 39.2 Hz, C-3), 126.8 (d, $^{1}J_{C,P}$ = 45.6 Hz, C-2), 128.6, 128.7, 131.1 (each s, *o*-, *m*-, *p*-C), 129.5 (d, $^{2}J_{C,P}$ = 6.8 Hz, *i*-C). – ^{31}P NMR ($CDCl_3$): δ = −247.1 (d, $^{1}J_{P,H}$ = 107 Hz). Compound **17** can also be obtained by reaction of **5a** with tributylstannane[24] or with lithium triethylborate[37].

Reactions of **5a** *with Sodium Borates* **18a–c**

2-tert-Butyl-1-ethyl-3-phenyl-1H-phosphirene [**19a** (≡**15g**)]: A solution of **5a** (0.16 g, 0.71 mmol) in diethyl ether (2 ml) was added at −78°C to a suspension of **18a** (0.11 g, 0.71 mmol) in diethyl ether (3 ml). After 15 min the reaction mixture was allowed to warm slowly to room temperature, the sodium chloride was removed by centrifugation, and the solvent removed by distillation in vacuum. Bulb-to-bulb distillation at 170°C/10^{-3} mbar yielded **19a** (≡**15g**) (0.07 g, 45%) as a colorless liquid. – Identification by IR and NMR comparison with **15g** which was obtained from **5a** and **14f**.

(2-tert-Butyl-1,3-diphenyl-1H-phosphirenium) Triphenylborate (**20a**): A mixture of the chloro-1*H*-phosphirene **5a** (0.28 g, 1.25 mmol) and sodium tetraphenylborate (**18b**) (0.43 g, 1.25 mmol) in deuteriotrichloromethane (3 ml) (reaction vessel: 10 mm NMR tube) was allowed to react at room temperature (^{31}P-NMR monitoring). When the starting material had disappeared, diethyl ether (5 ml) was added and the precipitated sodium chloride was removed by centrifugation. After removal of the solvent in vacuum the residue was recrystallized from diethyl ether/dichloromethane (1:1) at −20°C yielding **20a** as a colorless powder with m.p. 105°C. – ^{1}H NMR ($CDCl_3$): δ = 1.30 (s, 9H, *t*Bu), 7.0–7.9 (m, 25H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 29.9 [s, $C(CH_3)_3$], 34.4 [s, $C(CH_3)_3$], 115.1 (d, $^{1}J_{C,P}$ = 35.5 Hz, C-3), 127.6–138.3 (m, aromatic C), 136.0 (d, $^{1}J_{C,P}$ = 43.1 Hz, C-2), 141.5 (d, $^{1}J_{C,P}$ = 65.2 Hz, *i*-C-Ph-2), 144.8 (s, br., *i*-C-Ph-B). – ^{31}P NMR ($CDCl_3$): δ = −171.2. – $C_{36}H_{34}BP$ (508.5): calcd. C 85.04, H 6.74; found C 84.7, H 6.88.

2-tert-Butyl-1,3-diphenyl-1H-phosphirene (**19b**): Sodium tetraphenylborate (**18b**) (0.17 g, 0.49 mmol) was added to a solution of **5a** (0.11 g, 0.49 mmol) and pyridine (0.04 g, 0.49 mmol) in trichloromethane (3 ml) at room temperature. The reaction mixture was stirred for 90 min at the same temperature while the borate dissolved and a voluminous precipitate of pyridinium hydrochloride formed. The reaction mixture was filtered over Celite, the solvent was removed in vacuum, and the residue was extracted with pentane (5 ml). The pentane solution was again filtered and evaporated in vacuum. Bulb-to-bulb distillation at 190°C/10^{-3} mbar yielded **19b** (0.10 g, 76%) as a colorless oil. – ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 9H, *t*Bu), 7.0–7.7 (m, 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 29.7 [s, $C(CH_3)_3$], 33.9 [d, $^{2}J_{C,P}$ = 7.7 Hz, $C(CH_3)_3$], 114.3 (d, $^{1}J_{C,P}$ = 41.2 Hz, C-3), 127.7–130.8 (m, aromatic C), 135.9 (d, $^{1}J_{C,P}$ = 48.9 Hz, C-2), 143.3 (d, $^{1}J_{C,P}$ = 66.4 Hz, *i*-C-Ph-1). – ^{31}P NMR ($CDCl_3$): δ = −189.5. – $C_{18}H_{19}P$ (266.3): calcd. C 81.18, H 7.19; found C 81.0, H 7.2. Compound **19b** could also be detected in the reaction mixture by ^{31}P-NMR spectroscopy on treatment of the borane adduct, **20b**, with an equimolar amount of pyridine in deuteriotrichloromethane.

[2-tert-Butyl-1-(4-chlorophenyl)-3-phenyl-1H-phosphirenium [1-Tris(4-chlorophenyl)borate] (**20b**): A mixture of the chloro-1*H*-phosphirene **5a** (0.29 g, 1.30 mmol) and sodium tetrakis(4-chlorophenyl)borate (**18c**) (0.62 g, 1.30 mmol) in deuterio-trichloromethane (3 ml) (reaction vessel: 10 mm NMR tube) was allowed to react at room temperature (^{31}P-NMR monitoring). When the starting material could no longer be detected, diethyl ether (5 ml) was added and the precipitated sodium chloride was removed using a centrifuge. After removal of the solvent in vacuum **20b** (0.27 g, 30%) was isolated as a yellow powder. – ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 9H, *t*Bu), 6.8–7.6 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 29.8 [s, $C(CH_3)_3$], 34.5 [s, $C(CH_3)_3$], 115.5 (d, $^{1}J_{C,P}$ = 27.9 Hz, C-3), 126.7–137.9 (m, aromatic C), 135.6 (d, $^{1}J_{C,P}$ = 37.4 Hz, C-2), 136.9 (d, $^{1}J_{C,P}$ = 55.2 Hz, *i*-C-Ph-1), 145.0 (s, br., *i*-C-Ph-B). – ^{31}P-NMR ($CDCl_3$): δ = −173.2.

Reactions of **5a** *with Lithium Tetraalkoxyborates,* **18d–f**

General Procedure for the Synthesis of Lithium Tetraalkoxyborates, **18d–f**[61]: An equimolar amount of the trialkyl borate was added dropwise to a solution of *n*-butyllithium (9 ml, 15.00 mmol, 1.6 M solution in hexane) in diethyl ether (50 ml) at −78°C). The reaction mixture was allowed to warm to room temperature, and the precipitated crystals collected and washed several times with diethyl ether. Drying in vacuum yielded **18d–f** as colorless powders.

Lithium Tetramethoxyborate (**18d**): From trimethyl borate (1.56 g, 15.00 mmol). Yield: 1.70 g (80%). – ^{1}H NMR (CD_3OD): δ = 3.32 (s, OMe). – ^{11}B NMR (CD_3OD): δ = −12.5. $C_4H_{12}BLiO_4$ (141.9): calcd. C 33.86, H 8.52; found C 33.7, H 8.4.

Lithium Tetraethoxyborate (**18e**)[62]: From triethyl borate (2.19 g, 15.00 mmol). Yield: 2.31 g (78%). – ^{1}H NMR (CD$_3$OD): δ = 1.15 (d, $^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 3H, $\mathrm{OCH_2C}H_3$), 3.60 (q, $^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$). – ^{11}B NMR (CD$_3$OD): δ = –12.7. – $C_8H_{20}BLiO_4$ (198.0): calcd. C 48.53, H 10.18; found C 49.1, H 10.3.

Lithium Tetraisopropoxyborate (**18f**): From triisopropyl borate (2.89 g, 15.00 mmol). Yield: 2.70 g (71%). – ^{1}H NMR (CD$_3$OD): δ = 1.10 [d, $^{3}J_{\mathrm{H,H}}$ = 6.3 Hz, 6H, $\mathrm{OCH(C}H_3)_2$], 3.88 [sept, $^{3}J_{\mathrm{H,H}}$ = 6.3 Hz, 1H, $\mathrm{OC}H\mathrm{(CH_3)_2}$]. – ^{11}B NMR (CD$_3$OD): δ = –12.5. – $C_{12}H_{28}BLiO_4$ (245.1): calcd. C 56.72, H 11.01; found C 56.6, H 10.9.

General Procedure for the Synthesis of 1-Alkoxy-1H-phosphirenes **19d–f**: An equimolar amount of lithium tetraalkoxyborate was added to a solution of **5a** in diethyl ether (5 ml) at room temperature. The mixture was stirred for 1 h, the precipitated lithium chloride was removed using a centrifuge, and the solvent evaporated under vacuum. Bulb-to-bulb distillation of the residue yielded **19d–f** as colorless oils, which were analytically pure.

2-tert-Butyl-1-methoxy-3-phenyl-1H-phosphirene [**19d** (≡**15a**)]: From **5a** (0.32 g, 1.42 mmol) and lithium tetramethoxyborate (**18d**) (0.20 g, 1.42 mmol). Bulb-to-bulb distillation at 130°C/10^{-2} mbar yielded **19d** (0.24 g, 77%). Identification by NMR and comparison with **15a**, which was obtained from **5a** and **14a**.

2-tert-Butyl-1-ethoxy-3-phenyl-1H-phosphirene (**19e**): From **5a** (0.23 g, 1.02 mmol) and lithium tetraethoxyborate (**18e**) (0.21 g, 1.02 mmol). Bulb-to-bulb distillation at 150°C/10^{-2} mbar yielded **19e** (0.10 g, 45%). – ^{1}H NMR (CDCl$_3$). δ = 1.00 (t, $^{3}J_{\mathrm{H,H}}$ = 7.5 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.35 (s, 9H, *t*Bu), 3.30 (m, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.30–7.55 (m, 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 16.9 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 29.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.8 [d, $^{2}J_{\mathrm{C,P}}$ = 6.4 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 58.4 (s, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 128.7, 128.9, 130.3, 130.5 (each s, *o*-, *m*-, *p*-, *i*-C), 137.9 (d, $^{1}J_{\mathrm{C,P}}$ = 57.0 Hz, C-3), 154.8 (d, $^{1}J_{\mathrm{C,P}}$ = 63.9 Hz, C-2). – ^{31}P NMR (CDCl$_3$): δ = –82.9. – $C_{14}H_{19}OP$ (234.3): calcd. C 71.77, H 8.17; found C 71.6, H 8.2.

2-tert-Butyl-1-isopropoxy-3-phenyl-1H-phosphirene (**19f**): From **5a** (0.25 g, 1.10 mmol) and lithium tetraisopropoxyborate (**18f**) (0.28 g, 1.10 mmol). Bulb-to-bulb distillation at 145°C/10^{-3} mbar yielded **19f** (0.09 g, 33%). – ^{1}H NMR (CDCl$_3$): δ = 0.90, 1.00 [each d, $^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, each 3H, $\mathrm{OCH(C}H_3)_2$], 1.30 (s, 9H, *t*Bu), 3.70 [m, 1H, $\mathrm{OC}H\mathrm{(CH_3)_2}$], 7.2–7.7 (m, 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 24.3, 24.4 [each s, $\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$], 29.7 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 34.0 [d, $^{2}J_{\mathrm{C,P}}$ = 6.8 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 65.3 [s, $\mathrm{O}\mathit{C}\mathrm{H(CH_3)_2}$], 128.7, 128.9, 130.5 (each s, *o*-, *m*-, *p*-C), 129.9 (d, $^{2}J_{\mathrm{C,P}}$ = 6.9 Hz, *i*-C), 137.5 (d, $^{1}J_{\mathrm{C,P}}$ = 57.0 Hz, C-3), 154.2 (d, $^{1}J_{\mathrm{PC}}$ = 63.1 Hz, C-2). – ^{31}P NMR (CDCl$_3$): δ = –84.4. – MS (70 eV); *m/z* (%): 248 (71) [M^{+}], 205 (35), 189 (21), 158 (11), 143 (73), 128 (42), 77 (13), 57 (58). – $C_{15}H_{21}OP$ (248.3): calcd. C 72.56, H 8.52; found C 72.5, H 8.50.

Reaction of **5c** *with Sodium Tetramethoxyborate*

2-tert-Butyl-3-ethoxy-1-methoxy-1H-phosphirene (**19g**): To the solution of **5c** (0.09 g, 0.47 mmol) in trichloromethane was added sodium tetramethoxyborate (**18g**) (0.08 g, 0.47 mmol) at 0°C. The mixture was allowed to warm to room temperature, the precipitate was removed by filtration, and the solvent distilled under vacuum. Bulb-to-bulb distillation at 150°C/10^{-2} mbar yielded **19g** (0.04 g, 45%) as a colorless oil. – ^{1}H NMR (CDCl$_3$): δ = 1.23 (s, 9H, *t*Bu), 1.37 (t, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 3H, $\mathrm{OCH_2C}H_3$), 3.07 (d, $^{3}J_{\mathrm{H,P}}$ = 8.9 Hz, 3H, OCH$_3$), 4.20 (q, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$). – ^{13}C NMR (CDCl$_3$): δ = 15.3 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 29.5 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 31.6 [d, $^{2}J_{\mathrm{C,P}}$ = 5.1 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 49.3 (d, $^{2}J_{\mathrm{C,P}}$ = 5.6 Hz, $\mathrm{PO}\mathit{C}\mathrm{H_3}$), 69.9 (s, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 120.6 (d, $^{1}J_{\mathrm{C,P}}$ = 48.5 Hz, C-2), 153.9 (d, $^{1}J_{\mathrm{C,P}}$ = 69.1 Hz, C-3). – ^{31}P NMR (CDCl$_3$): δ = –40.0.

Reaction of **5** *with Trimethylsilyl Nucleophiles*

2-tert-Butyl-1-cyano-3-phenyl-1H-phosphirene (**22a**): A mixture of **5a** (0.48 g, 2.14 mmol) and trimethylsilyl cyanide (**21a**) (2.12 g, 21.37 mmol) was stirred at room temperature until the starting material, **5a**, could no longer by detected (^{31}P-NMR monitoring). After removal of trimethylsilyl chloride and excess trimethylsilyl cyanide in vacuum, the solid residue was recrystallized from dichloromethane/hexane at –25°C yielding **22a** (0.31 g, 67%) as colorless crystals; m.p. 81°C. – IR (film): ṽ = 2145 cm^{-1} (C≡N). – ^{1}H NMR (CDCl$_3$): δ = 1.48 (s, 9H, *t*Bu), 7.52, 7.78 (each m, 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 28.8 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.7 [d, $^{2}J_{\mathrm{C,P}}$ = 6.1 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 111.8 (d, $^{1}J_{\mathrm{PC}}$ = 44.6 Hz, C-3), 125.3 (d, $^{1}J_{\mathrm{PC}}$ = 181.0 Hz, C≡N), 125.7 (d, $^{2}J_{\mathrm{PC}}$ = 6.5 Hz, *i*-C), 127.1 (d, $^{1}J_{\mathrm{C,P}}$ = 51 Hz, C-2), 129.0, 130.2, 131.1 (each s, *o*-, *m*-, *p*-C). – ^{31}P NMR (CDCl$_3$): δ = –232.4. – $C_{13}H_{14}NP$ (215.2): calcd. C 72.55, H 6.58, N 6.52; found C 72.0, H 6.59, N 6.40.

2-tert-Butyl-1-cyano-3-ethoxy-1H-phosphirene (**22b**): A mixture of **5c** (0.11 g, 0.57 mmol) and trimethylsilyl cyanide (**21a**) (0.57 g, 5.75 mmol) was stirred at room temperature until the starting material, **5c**, could no longer be detected (^{31}P-NMR monitoring). Removal of trimethylsilyl chloride and excess trimethylsilyl cyanide in vacuum yielded **22b** (0.10 g, 100%) as a colorless oil. – IR (film): ṽ = 2150 cm^{-1} (C≡N). – ^{1}H NMR (CDCl$_3$): δ = 1.28 (s, 9H, *t*Bu), 1.43 (t, $^{3}J_{\mathrm{H(A)H(X)}}$ = $^{3}J_{\mathrm{H(B)H(X)}}$ = 7.15 Hz, X$_3$-part of an ABX$_3$-spin system, 3H, $\mathrm{OCH_2C}H_3$), 4.31 (m, AB-part of an ABX$_3$-spin system, 2H, $\mathrm{OC}H_2\mathrm{CH_3}$). – ^{13}C NMR (CDCl$_3$): δ = 15.4 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 28.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 31.2 [d, $^{2}J_{\mathrm{C,P}}$ = 6.5 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 71.7 (s, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 89.0 (d, $^{1}J_{\mathrm{C,P}}$ = 35.2 Hz, C-2), 125.2 (d, $^{1}J_{\mathrm{C,P}}$ = 193.5 Hz, C≡N), 130.3 (d, $^{1}J_{\mathrm{C,P}}$ = 52.5 Hz, C-3). – ^{31}P NMR (CDCl$_3$): δ = –182.0. – MS (70 eV); *m/z* (%): 183 (4) [M^{+}], 168 (3), 157 (14), 154 (22), 140 (4), 128 (21), 113 (3), 110 (13), 57 (100), 41 (21), 29 (19), 27 (8).

1-Azido-2-tert-butyl-3-phenyl-1H-phosphirene (**22c**): A mixture of **5a** (0.56 g, 2.50 mmol) and trimethylsilyl azide (**21b**) (2.88 g, 5.75 mmol) was stirred at room temperature until the starting material, **5a**, could no longer be detected (^{31}P-NMR monitoring). Removal of trimethylsilyl chloride and excess trimethylsilyl azide in vacuum yielded **22c** (0.58 g, 100%) as a colorless oil. – IR (film): ṽ = 2090 cm^{-1} (N=N=N). – ^{1}H NMR (CDCl$_3$): δ = 1.45 (s, 9H, *t*Bu), 7.60 (m, 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 29.4 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 33.5 [d, $^{2}J_{\mathrm{C,P}}$ = 6.2 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 128.1 (d, $^{2}J_{\mathrm{C,P}}$ = 6.8 Hz, *i*-C), 129.1, 130.1, 131.0 (each s, *o*-, *m*-, *p*-C), 130.5 (d, $^{1}J_{\mathrm{C,P}}$ = 66.3 Hz, C-3), 146.6 (d, $^{1}J_{\mathrm{C,P}}$ = 62.8 Hz, C-2). – ^{31}P NMR (CDCl$_3$): δ = –106.7. – $C_{12}H_{14}N_3P$ (231.2): calcd. C 62.33, H 6.10, N 18.17; found C 62.2, H 6.15, N 16.1.

1-Azido-2,3-di-tert-butyl-1H-phosphirene (**22d**): A mixture of **5b** (0.52 g, 2.50 mmol) and trimethylsilyl azide (**21b**) (2.88 g, 5.75 mmol) was stirred at room temperature until the starting material, **5b**, could no longer be detected (^{31}P-NMR monitoring). Removal of trimethylsilyl chloride and excess trimethylsilyl azide in vacuum yielded **22d** (0.49 g, 100%) as a colorless oil. – IR (film): ṽ = 2100 cm^{-1} (N=N=N). – ^{1}H NMR (CDCl$_3$): δ = 1.28 (s, 18H, *t*Bu). – ^{13}C NMR (CDCl$_3$): δ = 30.0 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 32.6 [d, $^{2}J_{\mathrm{C,P}}$ = 6.3 Hz, $\mathit{C}\mathrm{(CH_3)_3}$], 142.9 (d, $^{1}J_{\mathrm{C,P}}$ = 61.3 Hz, C-2/C-3). – ^{31}P NMR (CDCl$_3$): δ = –106.3.

Reactions of **22a, d** *with Pentacarbonyltungsten · Tetrahydrofuran – General Procedure:* A solution of pentacarbonyltungsten · THF was prepared by irradiation of a solution of hexacarbonyltungsten in THF (HPK, 125 W, Philips) for 30 min. This solution was added to **22** in THF (5 ml) and the mixture was stirred for 3 h at room temperature. The solvent and all volatile compounds were then removed by distillation in vacuum. The residue was taken up in pentane (about 50 ml), filtered, and the pentane evaporated in vacuum. The work-up was continued as described below for the individual compounds.

(η^1-2-tert-Butyl-1-cyano-3-phenyl-1H-phosphirene-P)pentacarbonyltungsten (**23**): From hexacarbonyltungsten (0.53 g, 1.51 mmol) and 1-cyano-1*H*-phosphirene **22a** (0.28 g, 1.30 mmol). Medium-pressure liquid chromatography (MPLC, Büchi 681, 46 × 3.6 cm, pressure 40 bar, silica gel 60, Merck) with hexane/diethyl ether (2:1) yielded two fractions. Further MPLC of the second fraction yielded, after removal of the solvents in vacuum, **23** (0.09 g, 13%) as a yellow solid which was recrystallized from pentane/diethyl ether (1:2); m.p. 131°C (dec.). – IR (pentane solution): $\tilde{\nu}$ = 2167 ($C\equiv N$), 2079, 1994, 1950 cm^{-1} ($C\equiv O$). – ^{1}H NMR ($CDCl_3$): δ = 1.53 (s, 9H, *t*Bu), 7.58, 7.76 (each m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.3 [d, $^{3}J_{C,P}$ = 3.3 Hz, $C(CH_3)_3$], 34.0 [d, $^{2}J_{C,P}$ = 4.8 Hz, $C(CH_3)_3$], 120.5 (d, $^{1}J_{C,P}$ = 71.2 Hz, $C\equiv N$), 122.4 (d, $J_{C,P}$ = 13.4 Hz, C-3), 123.9 (d, $^{2}J_{C,P}$ = 5.2 Hz, *i*-C), 129.6, 131.6, (each s, *o*-, *p*-C), 130.9 (d, $^{4}J_{C,P}$ = 6.7 Hz, *m*-C), 135.2 (d, $^{1}J_{C,P}$ = 19.1 Hz, C-2), 194.0 (d, $^{2}J_{C,P}$ = 8.5 Hz, $^{1}J_{C,W}$ = 126.0 Hz, $C\equiv O_{equatorial}$), 195.7 (d, $^{2}J_{PC}$ = 42.1 Hz, $C\equiv O_{axial}$). – ^{31}P NMR ($CDCl_3$): δ = –209.4 ($^{1}J_{P,W}$ = 312.4 Hz). – $C_{18}H_{14}NO_5PW$ (539.1): calcd. C 40.10, H 2.62, N 2.60; found C 39.5, H 2.62, N 2.40. – Flash chromatography (20 × 3.5 cm, silica gel 60, Merck) with hexane/toluene instead of medium-pressure chromatography of the crude product yielded, after removal of the solvent in vacuum and recrystallization from pentane/diethyl ether, **24** (0.10 g, 9%) as yellow crystals with m.p. 115°C (dec.); on the basis of spectroscopic data, **24** corresponds in all respects to the substance obtained by the reaction of **22a** with pentacarbonyltungsten · THF in a molar ratio of 1:2; see below.

(η^1,η^1-2-tert-Butyl-1-cyano-3-phenyl-1H-phosphirene-N,P)-di(pentacarbonyltungsten) (**24**): From hexacarbonyltungsten (1.06 g, 3.01 mmol) and cyano-1*H*-phosphirene **22a** (0.31 g, 1.44 mmol). The residue was taken up in pentane (20 ml) and cooled to –30°C yielding **24** (041 g, 33%) as yellow crystals with m.p. 115°C (dec.). – IR (hexane solution): $\tilde{\nu}$ = 2149 ($C\equiv N$), 2083, 2066, 1965, 1946, 1932 cm^{-1} ($C\equiv O$). – ^{1}H NMR ($CDCl_3$): δ = 1.56 (s, 9H, *t*Bu), 7.63, 7.78 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.7 [d, $^{3}J_{C,P}$ = 3.0 Hz, $C(CH_3)_3$], 34.3 [d, $^{3}J_{C,P}$ = 4.8 Hz, $C(CH_3)_3$], 122.5 (d, $^{1}J_{C,P}$ = 15.1 Hz, C-3), 123.3 (d, $^{2}J_{C,P}$ = 5.6 Hz, *i*-C), 128.6 (d, $^{1}J_{C,P}$ = 83.8 Hz, $C\equiv N$), 129.8, 132.1 (each s, *o*-, *p*-C), 131.0 (d, $^{4}J_{C,P}$ = 6.6 Hz, *m*-C), 135.6 Hz, (d, $^{1}J_{C,P}$ = 20.8 Hz, C-2), 193.6 (d, $^{2}J_{C,P}$ = 8.2 Hz, $^{1}J_{C,W}$ = 126.0 Hz, $C\equiv O_{equatorial}$), 195.0 (d, $^{2}J_{C,P}$ = 43.7 Hz, $C\equiv O_{axial}$), 195.6 (s, $^{1}J_{C,W}$ = 130.5 Hz, $C\equiv O_{equatorial}$), 198.8 (s, $^{1}J_{C,W}$ = 152.6 Hz, $C\equiv O_{axial}$). – ^{31}P NMR ($CDCl_3$): δ = –200.5 ($^{1}J_{P,W}$ = 317.3 Hz).

(η^1-1-Azido-2,3-di-tert-butyl-1H-phosphirene-P)-pentacarbonyltungsten (**25**): From hexacarbonyltungsten (0.86 g, 2.20 mmol) and **22d** (0.41 g, 2.00 mmol). Recrystallization of the crude product from toluene at –78°C yielded **25** (0.12 g, 11%) as yellow-brown crystals. – IR (film): $\tilde{\nu}$ = 2120 (N=N=N), 1985, 1954 cm^{-1} ($C\equiv O$). – ^{1}H NMR ($CDCl_3$): δ = 135 (s, 18H, *t*Bu). – ^{31}P NMR ($CDCl_3$): δ = –106.0 ($^{1}J_{P,W}$ = 315.1 Hz). – $C_{15}H_{18}N_3O_5PW$ (535.1): calcd. C 33.66, H 3.38, N 7.85; found C 33.8, H 3.45, N 7.5.

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