Synthesis and Reactions of (1,1′-Bi-1*H*-phosphirene)iron Complexes − Crystal Structure of a Bridged (1-Phosphaallyl-1*H*-phosphirene)diiron(*Fe*−*Fe*) Complex[‡]

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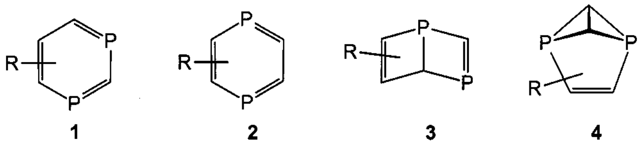
The reactions of 1-chloro-1*H*-phosphirenes **5** with disodium tetracarbonlyferrate lead to the selective formation of the mono complexed bi-1*H*-phosphirenes **7**, which are converted into the doubly complexed species **9** upon treatment with diiron nonacarbonyl. Photochemical opening of one of the two three-membered ring systems in **9** furnishes the bridged complexes **10** containing phosphirene and phosphaallyl units together with an iron-iron σ-bond.

Introduction

Since the 1960's investigations on the synthesis and reactivity of phosphinines and their valence isomers have played a significant role in the development of the chemistry of low-coordinated phosphorus compounds.[2−5] In contrast, the only known representatives of diphosphinines are the 1,3[6] and 1,4 derivatives[7] **1** and **2** (Scheme 1). Recently, an access to valence isomers of the 1,3-diphospha-Dewar-benzene **3** and diphosphabenzvalene **4** types was established using specific trapping reactions of a short-lived 1,3-diphosphacyclobutadiene with suitably substituted alkynes.[8] 1,3-Diphosphinines **1** are also able to undergo a valence isomerization to the Dewar isomers on prolonged heating.[6c]



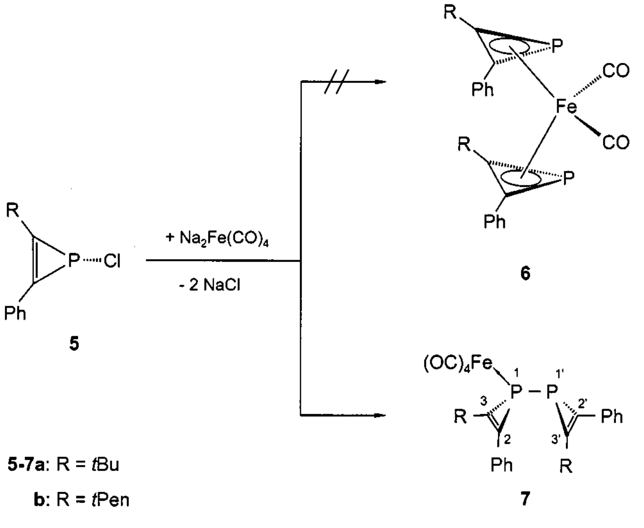
Scheme 1

In the present report, we described the synthesis of the iron complexed 1,1′-bi-1*H*-phosphirenes **7** and **9** as a further, previously unknown class of valence isomers of the diphosphinines.[9] Very recently, the corresponding 1,1′-bisilacyclopropenes, the valence isomers of 1,4-disilabenzenes, have also been synthesized.[10]

Results and Discussion

Synthesis of the (1,1′-Bi-1*H*-phosphirene)iron Complexes 7a and 7b

In the reactions of the 1-chloro-1*H*-phosphirenes **5** with disodium tetracarbonylferrate, the mono η^1 complexed 1,1′-bi-1*H*-phosphirenes **7a** and **7b** (58 and 60%) are formed highly selectively (Scheme 2), instead of the expected $\eta^{3:3}$-(bisphosphirenylium)dicarbonyliron complexes **6**.



Scheme 2

Elemental analysis and mass spectroscopic data unequivocally demonstrate that the complexes **7a** and **7b** are 2:1 adducts of the 1-chloro-1*H*-phosphirenes **5a** and **5b** with Collman's reagent, formed under concomitant loss of two molecules of sodium chloride.

Mixtures of two diastereomers that cannot be separated by column chromatography are obtained. One diastere-

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[‡] Organophosphorus Compounds, 154. − Part 153: Ref.[1]

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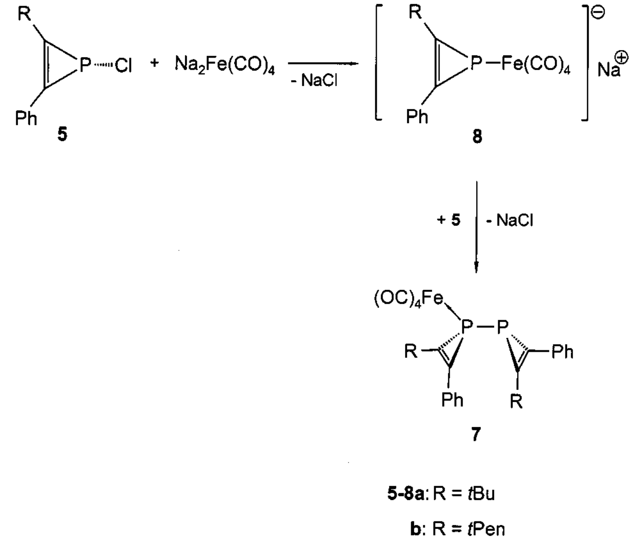
omer, however, can be enriched up to a ratio of 8:1 (**7a**) or 4:1 (**7b**) (as determined by ^{1}H NMR spectroscopy) by crystallization. The NMR spectroscopic data provide diagnostic information for the structure elucidation, as discussed below for the example of **7a** (major diastereomer; R = *t*Bu).

The formation of this product is demonstrated by its ^{31}P NMR spectrum, which reveals a significant, large $^1J_{P,P}$ coupling constant of 427.3 Hz. The signal at $\delta = -88.1$ is assigned to the iron complexed phosphorus atom P-1 by comparison with the published values for iron complexed 1*H*-phosphirenes[11], while the signal at higher field ($\delta = -134.2$) originates from the non-complexed phosphirene unit.

A conspicuous feature of the ^{13}C NMR spectrum of **7a** is a drastic reduction of the intracyclic carbon/phosphorus coupling constants in the complexed three-membered ring ($^1J_{C,P}$ = 22.0 and 27.1 Hz) in comparison with those of the non-complexed three-membered ring ($^1J_{C,P}$ = 50.8 and 57.7 Hz). This is a generally observed phenomenon on going from three- to four-coordinated 1*H*-phosphirenes.[12] The chemical shifts of the alkyl- and aryl-substituted ring carbon atoms are also in agreement with literature data.[13] The resonance signals at lower field (δ = 140.5 and 138.5) are attributed to the alkyl-substituted carbon atoms C-3 and C-3′ while the phenyl-substituted C atoms C-2 and C-2′ give rise to the signals at markedly higher field (δ = 124.8 and 120.3).

The formation of **7a** and **7b** must proceed through a multi-step sequence, although ^{31}P NMR monitoring of the reaction mixture did not provide any indications for the existence of intermediates (Scheme 3).

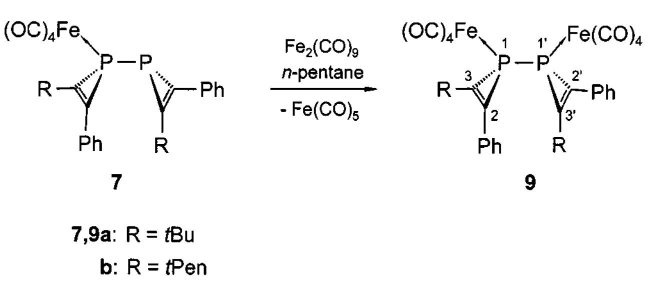


Scheme 3

A plausible mechanism involves the substitution of the chlorine atom in **5** by an anionic tetracarbonyliron fragment to afford the anionic 1*H*-phosphirene complex **8**. This complex then undergoes an immediate nucleophilic substitution with a further molecule of **5** to afford the mono complexed 1,1′-bi-1*H*-phosphirenes **7**.

Further Complexation of (1,1′-Bi-1*H*-phosphirene)iron Complexes 7a and 7b with Diironnonacarbonyl To Afford (1,1′-Bi-1*H*-phosphirene)diiron Complexes 9a and 9b

The additional complexation of the free phosphorus atom provides a possibility to improve the crystallization properties of the novel diphosphinine valence isomers **7**. Reactions of **7** with a slight excess of diiron nonacarbonyl proceed selectively to afford the (1,1′-bi-1*H*-phosphirene)diiron complexes **9** carrying two tetracarbonyliron fragments (Scheme 4). After workup by column chromatography and subsequent recrystallization from *n*-pentane the binuclear complexes **9a** and **9b** are obtained in good yields (63% and 54%, respectively) in the form of yellow-orange crystals.



Scheme 4

Elemental analysis and mass spectroscopic data unequivocally confirm the presence of two Fe(CO)$_4$ fragments in **9a** and **9b**. The NMR spectroscopic data of these complexes are highly simplified, and discussed for the example of the main diastereomer **9a**.

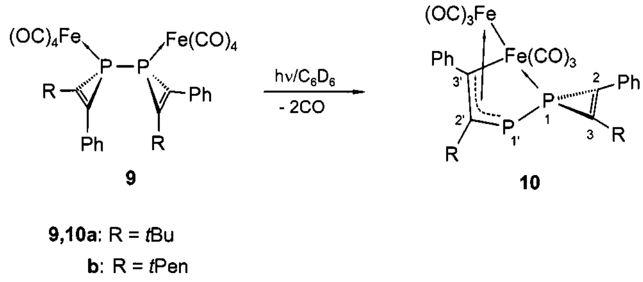
The magnetically equivalent phosphorus atoms P-1 and P-1′ in **9a** give rise to a singlet signal in the ^{31}P NMR spectrum at $\delta = -69.3$. In comparison to the spectrum of **7a** the additional complexation results in a pronounced deshielding by 64.9 ppm of the ^{31}P NMR signals of the formerly non-coordinated phosphorus.

The ^{13}C NMR spectrum of **9a** reflects the double complexation by the appearance of pseudo-triplet signals for the carbonyl and ring carbon atoms. Furthermore, the intracyclic phosphorus-carbon coupling constants of the 1*H*-phosphirene unit that was not complexed in **7a** are, as expected, drastically reduced as a result of the complexation with the second tetracarbonyliron fragment. In analogy with compound **7**, the signals for the ring carbon atoms seen at lower field are assigned to the alkyl-substituted carbon atoms C-3 and C-3′ (δ = 142.2). Similar to the ^{31}P NMR spectroscopic data of **9a** and **9b**, the ^{13}C NMR signals of the ring carbon atoms also experience a clear shift to lower field as a result of the additional complexation.

Final confirmation of the structure of the iron complexed 1,1′-bi-1*H*-phosphirene **9a** was obtained by X-ray crystallography.[9]

Photolyses of the (1,1′-Bi-1*H*-phosphirene)diiron Complexes 9a and 9b To Give the (1-Phosphaallyl-1*H*-phosphirene)-diiron(*Fe*−*Fe*) Complexes 10a and 10b

Previously, only a single example of a photochemically induced rig opening reaction of a complexed 1*H*-phosphirene was known.[14] When a solution of the doubly complexed 1,1′-bi-1*H*-phosphirenes **9a** or **9b** in C_6D_6 is irradiated in an NMR tube using a 125 W high-pressure mercury lamp, ^{31}P NMR monitoring of the mixture reveals a relatively unselective reaction sequence (Scheme 5). After workup by column chromatography and subsequent recrystallization from *n*-pentane/diethyl ether, the pure compounds **10a** or **10b** are isolated only in low yields (5 and 6%, respectively).



Scheme 5

Elemental analysis and mass spectroscopic data unambiguously demonstrate the cleavage of two carbonyl groups from **9a** and **9b**. The NMR spectroscopic data also provide diagnostic information on the constitutions of compounds **10a** and **10b**.

The ^{31}P NMR spectra, discussed here for the example of **10a**, contains two doublets at $\delta = -1.6$ and -70.4. Of these, the signal at higher field is only shifted slightly in comparison to that of the starting compound **9a**, thus confirming the retention of one of the two 1*H*-phosphirene units. On the other hand, the low-field shift of the other doublet indicates that the second three-membered ring unit has been opened. This signal can be assigned to a (1-phosphaallyl)iron complex by comparison with published values for structural increments of this type.[15]

The $^{13}C\{^1H\}$ NMR spectrum of **10a** is in agreement with the proposed structure, and contains 8 different signals in addition to those of the aryl and alkyl substituents. Although only one doublet at $\delta = 212.4$ with a coupling constant of 6.8 Hz is observed for one of the two $Fe(CO)_3$ groups, a doublet signal with an appreciably larger carbon-phosphorus coupling constant of 27.1−28.8 Hz is found for each CO ligand of the second transition metal fragment. The occurrence of different signals for the carbonyl ligands of this $Fe(CO)_3$ group confirms a hindered exchange between the axial and equatorial positions of the carbonyl ligands. Since the η^3-coordination of the 1-phosphaallyl fragment creates high steric demands, these signals may safely be assigned to the tricarbonyliron fragment of this structural increment.

The carbon atoms C-2′ and C-3′of the 1-phosphaallyl element give rise to signals at $\delta = 191.2$ and 153.9. Since the signal at lower field is split into a double doublet it is assigned to the C-2′ atom directly bonded to phosphorus. The extremely low-field position of this signal is also characteristic for a P=C double bond system. The bridging carbon atom C-3′ of **10a**, on the other hand, gives a signal at appreciably higher field. A comparison of the chemical shift of this carbon atom (C-3′; $\delta = 153.9$) with the published values for bridged allyl complexes[16] provides further support for this structure. The signals of the ring carbon atoms C-2 and C-3 are found at $\delta = 150.6$ (C-3) and $\delta = 124.6$ (C-2) in the region typical for 1*H*-phosphirenes with this substitution pattern. The chemical shifts have been assigned analogously to those for compounds **7** and **9**. Although the $^{13}C\{^1H\}$ NMR signals of the phenyl substituents cannot be assigned individually, this is possible for the alkyl substituents. As expected, two sets of signals are observed for the two *tert*-butyl groups, with one of the signal sets being markedly shifted to lower field. By comparison with the values for other allyl complexes,[15] the signals at lower field are attributed to the alkyl substituents at C-2′.

This low-field signal shift of the substituents of the phosphaallyl unit is also observed in the ^1H NMR spectrum of **10a**. Thus, the *tert*-butyl group at C-2′ gives rise to a signal at $\delta = 1.42$, while the alkyl substituent of the phosphirene ring produces a signal at $\delta = 1.16$. The signals of the protons of the phenyl groups overlap, resulting in the observation of only a multiplet in the typical aromatic proton region.

The structure of **10a** was finally and irrevocably confirmed by X-ray crystallography (Figure 1).

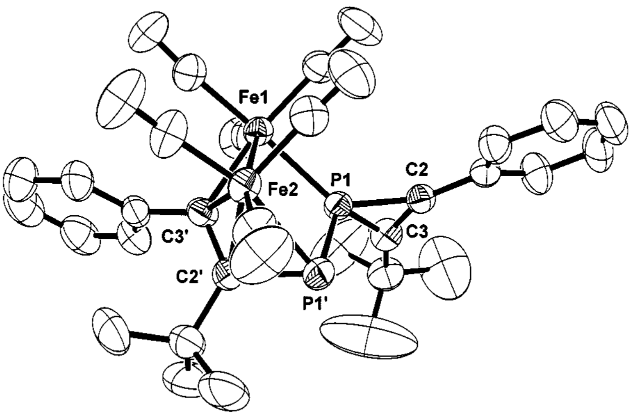
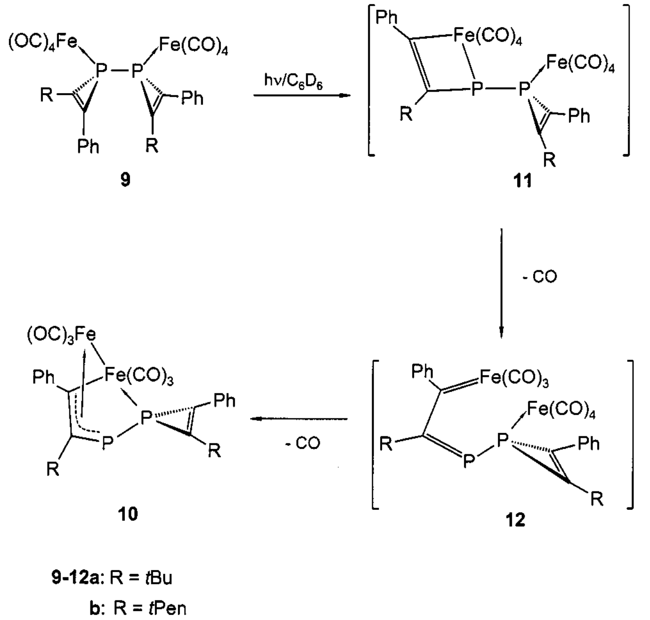


Figure 1. Molecular structure of **10a**. Selected bond lengths [Å] and angles [°]: Fe(1)−C(3′) 2.037(3), Fe(1)−P(1) 2.2078(9), Fe(1)−Fe(2) 2.6493(6), Fe(2)−C(3′) 2.102(3), Fe(2)−C(2′) 2.135(3), Fe(2)−P(1′) 2.3684(12), P(1)−C(2) 1.773(3), P(1)−C(3) 1.795(3), P(1)−P(1′) 2.1597(11), P(1′)−C(2′) 1.811(3), C(2)−C(3) 1.341(4), C(2′)−C(3′) 1.445(4); C(3′)−Fe(1)−P(1) 83.08(10), C(3′)−Fe(2)−C(2′) 39.87(12), C(3′)−Fe(2)−P(1′) 76.14(10), C(2′)−Fe(2)−P(1′) 47.07(8), C(2)−P(1)−C(3) 44.16(14), C(2)−P(1)−P(1′) 115.28(10), C(3)−P(1)−P(1′) 118.56(11), C(2′)−P(1′)−P(1) 92.56(10), C(3)−C(2)−P(1) 68.82(18), C(2)−C(3)−P(1) 67.0(2), C(3′)−C(2′)−P(1′) 115.8(2), C(2′)−C(3′)−Fe(1) 125.2(2)

The resultant ORTEP plot clearly reveals the opening of one of the two phosphirene rings with formation of an η^3 complexed 1-phosphaallyl system. The crystal structure analysis also confirms the formation of an iron-iron single bond (see below), as well as the retention of the second phosphirene ring. The Fe1−P1 bond length of 2.208(9) Å is in the typical range for an iron complexed phosphane,[17] and is comparable with the iron-phosphorus bond length in **9a**. On the other hand, the Fe−P1′ bond length in the 1-phosphaallyl unit of 2.368(1) Å is appreciably stretched in comparison with those of other η^3-phosphaallyl-iron complexes.[15] This is readily explained by the steric requirements of the substituents that force the $Fe(CO)_3$ fragment away from the 1-phosphaallyl unit. The iron-carbon separations in this structural increment are almost identical to those in a comparable compound formed by the reaction the μ_3-RP bridged cluster $(\mu_3\text{-RP})Fe_3(CO)_{10}$ with terminal alkynes.[15] The bond lengths in the phosphaallyl unit of 1.811(3) Å (P1′−C2′) and 1.445(4) Å (C2′−C3′) are clearly lengthened, and are of magnitudes typical for single bonds. This is probably due to the enormous spatial requirements of the substituents. The iron−iron bond length of 2.6493(6) Å in **10a** is also of a typical magnitude for this type of single bond.[15] The P1−P1′-bond length of 2.159(1) Å is considerably shortened in comparison with those of uncomplexed phosphanes or that of **9a**.[18] This observation can be rationalized by the ring-bracketing effect of the Fe−C-3′ bond. The intracyclic bonding parameters of the intact phosphirene ring of **10a** are in the typical ranges for a transition-metal complexed 1*H*-phosphirene.[12]

On the basis of $^{31}P\{^1H\}$ NMR monitoring of the photolysis reaction of **9a** a multi-step sequence can be assumed. By comparison of the resonance signals of the various intermediates with those of known compounds, the following mechanism can be proposed:

The initial step in the formation of **10** could be the insertion of one of the two $Fe(CO)_4$ fragments into a P−C bond of the coordinatively attached three-membered ring systems. This results in the intermediate **11**, in which a metallaphosphacyclobutene system is linked to a complexed phosphirene system (Scheme 6). The signal for the phosphorus atom in the three-membered ring of **11a** appears in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution as a doublet at $\delta = -99.5$ ($^1J_{P,P} = 322.4$ Hz). A further doublet with the same coupling constant is seen at $\delta = 56.0$. This chemical shift value is typical for a compound with a metallaphosphacyclobutene skeleton as revealed by a comparison with an analogous rhodium complex.[19] The subsequent cleavage of a carbonyl ligand from the $Fe(CO)_4$ fragment of the four-membered ring then initiates the conversion of the η^2-coordinated complex **11** with ring opening to the 16-valence electron carbene complex **12**. The P=C double bond of the phosphaalkene system in **12a** gives rise to a $^{31}P\{^1H\}$ NMR signal at $\delta = 282.1$. This value is in the typical range for a phosphaalkene. Since the 16-VE fragment in **12** is coordinatively unsaturated and thus possesses only a low stability, subsequent rearrangement occurs with cleavage of a CO ligand and formation of an Fe−C σ-bond and the Fe−Fe single bond.



Scheme 6

Experimental Section

General Remarks: The reactions were carried out under an atmosphere of argon (purity > 99.998%) in a previously baked-out and evacuated apparatus (Schlenk techniques). The solvents were dried by standard procedures (*n*-pentane and diethyl ether: Na/K alloy), distilled and stored under argon. − Melting points: Mettler FP 61 (heating rate: 3 °C/min). − FT-IR spectra: Perkin−Elmer infrared-spectrometer 16PC. − Mass spectra: Finnigan MAT 90 spectrometer. − NMR spectra: Bruker AMX 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) and Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz, ^{31}P: 81 MHz) spectrometers, solvent as internal standard (^{1}H and ^{13}C); the chemical shifts for ^{31}P are relative to external 85% orthophosphoric acid. − Compounds **5a** and **5b** were prepared by published methods.[13] Disodium tetracarbonylferrate was purchased from Aldrich and used without further purification.

Column chromatography was formed in water-cooled glass tubes with a positive pressure of argon on the column. Silica gel and neutral aluminum oxide were heated for 5 h under vacuum and then deactivated with 4% water.

Synthesis of the (1,1′-Bi-1*H*-phosphirene)iron Complexes 7a and 7b. − General Procedure: To a suspension of disodium tetracarbonylferrate in diethyl ether (30 mL) was added dropwise with stirring at −78 °C a solution of two equivalents of the corresponding 1-chloro-1*H*-phosphirene **5** in diethyl ether (20 mL). The reaction mixture was allowed to warm up to room temp. with stirring. The mixture was then evaporated under vacuum and the residue purified by column chromatography on silica gel with *n*-pentane/diethyl ether [40:1 (**7a**), 100:1 (**7b**)] as eluent. The yellow eluate was evaporated to dryness and the resulting red solid was recrystallized from *n*-pentane at −28 °C to yield pure **7** as orange-yellow crystals.

[3,3′-Bis(1,1-dimethylethyl)-2,2′-diphenyl-1,1′-bi-1*H*-phosphirene-κ*P*^{1}]tetracarbonyliron (7a): Starting materials: 791 mg (3.52 mmol)

1-chloro-3-(1,1-dimethylethyl)-2-phenyl-1*H*-phosphirene (**5a**), 609 mg (1.76 mmol) disodium tetracarbonylferrate. − Yield 560 mg (58%), orange-yellow crystals, mixture of two diastereomers (ratio 8:1). − m.p.: 97 − 99 °C. − IR (CCl_4, cm^{-1}): $\tilde{\nu}$ = 2966 (w), 2042 (s, CO), 1971 (m, CO), 1939 (vs, CO), 1474 (w), 1072 (m), 1008 (m), 620 (s). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): *major diastereomer*: δ = −88.1 (d, $^1J_{P,P}$ = 427.3 Hz, P-1), −134.2 (d, $^1J_{P,P}$ = 427.3 Hz, P-1′); *minor diastereomer*: δ = −86.8 (d, $^1J_{P,P}$ = 427.1 Hz, P-1), −132.6 (d, $^1J_{P,P}$ = 427.1 Hz, P-1′). − ^1H NMR ($CDCl_3$): *major diastereomer*: δ = 1.44 [s, broad, 18 H, $C(CH_3)_3$]; *minor diastereomer*: δ = 1.50 [s, broad, 18 H, $C(CH_3)_3$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): not all signals could be assigned because of overlapping effects: *major diastereomer:* δ = 29.2 [d, $^3J_{C,P}$ = 1.7 Hz, $C(CH_3)_3$], 29.5 [s, $C(CH_3)_3$], 33.9 [dd, $^2J_{C,P}$ = 6.4 Hz, $^3J_{C,P}$ = 3.0 Hz, $C(CH_3)_3$], 34.2 [d, $^2J_{C,P}$ = 6.8 Hz, $C(CH_3)_3$], 120.3 (d, $^1J_{C,P}$ = 50.8 Hz, C-2′), 124.8 (dd, $^1J_{C,P}$ = 22.0 Hz, $^2J_{C,P}$ = 4.2 Hz, C-2), 127.3 (d, $J_{C,P}$ = 7.6 Hz, Ph), 128.6 (s, Ph), 128.9 (s, Ph), 129.7 (d, $J_{C,P}$ = 5.1 Hz, Ph), 130.4 (d, $J_{C,P}$ = 4.2 Hz, Ph), 131.3 (s, Ph), 138.5 (d, $^1J_{C,P}$ = 57.7 Hz, C-3′), 140.5 (dd, $^1J_{C,P}$ = 27.1 Hz, $^2J_{C,P}$ = 5.1 Hz, C-3), 213.9 (d, $^2J_{C,P}$ = 19.5 Hz, CO); *minor diastereomer*: δ = 29.2 [s, $C(CH_3)_3$], 29.4 [d, $^3J_{C,P}$ = 2.5 Hz, $C(CH_3)_3$], 34.3 [d, $^2J_{C,P}$ = 5.9 Hz, $C(CH_3)_3$], 121.3 (dd, $^1J_{C,P}$ = 48.9 Hz, $^2J_{C,P}$ = 2.6 Hz, C-2′), 125.0 (dd, $^1J_{C,P}$ = 33.7 Hz, $^2J_{C,P}$ = 3.4 Hz, C-2), 127.2 (d, $J_{C,P}$ = 11.0 Hz, Ph), 128.6 (s, Ph), 129.7 (d, $J_{C,P}$ = 5.1 Hz, Ph), 130.3 (d, $J_{C,P}$ = 4.2 Hz, Ph), 131.2 (s, Ph), 135.6 (d, $^1J_{C,P}$ = 56.2 Hz, C-3′), 141.8 (dd, $^1J_{C,P}$ = 26.3 Hz, $^2J_{C,P}$ = 4.2 Hz, C-3), 214.2 (d, $^2J_{C,P}$ = 18.7 Hz, CO). − MS (EI, 70 eV): *m*/*z* (%) = 546 (8) [M^+], 434 (41) [M^+ − 4CO], 276 (100) [M^+ − 4CO − $C_{12}H_{14}$], 98 (43) [$C_2P_2Fe(CO)_2^+$], 189 (68) [$C_{12}H_{14}P^+$], 143 (26) [$C_{11}H_{11}^+$]. − $C_{28}H_{28}FeP_2O_4$ (546.32 g/mol): calcd. C 61.56, H 5.17; found C 60.90, H 5.07. − HR-MS (EI, 70 eV); [M^+]: calcd. 546.0813; found 546.0813.

[3,3′-Bis(1,1-dimethylpropyl)-2,2′-diphenyl-1*H*-phosphirene-κ*P*¹]-tetracarbonyliron (7b): Starting materials: 649 mg (2.72 mmol) 1-chloro-3-(1,1-dimethylpropyl)-2-phenyl-1*H*-phosphirene (**5b**), 471 mg (1.36 mmol) disodium tetracarbonylferrate. − Yield 470 mg (60%), orange-yellow solid, mixture of two diastereomers (ratio 4:1). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2967 (s), 2934 (w), 2039 (vs, CO), 1963 (s, CO), 1938 (vs, CO), 1636 (m), 1464 (m), 1074 (s), 620 (s). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): *major diastereomer*: δ = −90.6 (d, $^1J_{P,P}$ = 427.6 Hz, P-1), −132.2 (d, $^1J_{P,P}$ = 427.6 Hz, P-1′); *minor diastereomer*: δ = −88.3 (d, $^1J_{P,P}$ = 426.6 Hz, P-1), −132.3 (d, $^1J_{P,P}$ = 426.6 Hz, P-1′). − ^1H NMR ($CDCl_3$): *major diastereomer:* δ = 0.96 (t, 3 H, $^3J_{H,H}$ = 7.6 Hz, CH_2-CH_3), 1.12 (t, 3 H, $^3J_{H,H}$ = 7.0 Hz, CH_2-CH_3), 1.42, 1.43, 1.46, 1.47 [each s, 12 H, $C(CH_3)_2CH_2$], 1.63 − 1.92 (m, 4 H, CH_2-CH_3; *minor diastereomer:* the signals could not be assigned because of overlapping effects. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): not all signals could be assigned because of overlapping effects: *major diastereomer:* δ = 8.7 (d, $^4J_{C,P}$ = 6.3 Hz, CH_2-CH_3), 9.1 (d, $^4J_{C,P}$ = 4.5 Hz, CH_2-CH_3), 25.7 [s, $C(CH_3)_2$], 26.2 [d, $^3J_{C,P}$ = 5.4 Hz, $C(CH_3)_2$], 26.5 [s, $C(CH_3)_2$], 26.9 [s, $C(CH_3)_2$], 34.4 (d, $^3J_{C,P}$ = 5.4 Hz, CH_2-CH_3), 34.4 (s, CH_2-CH_3), 37.0 [s, $C(CH_3)_2$Et], 37.7 [d, $^2J_{C,P}$ = 5.4 Hz, $C(CH_3)_2$Et], 120.9 (d, $^1J_{C,P}$ = 51.2 Hz, C-2′), 125.1 (d, $^1J_{C,P}$ = 22.4 Hz, C-2), 127.0 (d, $^3J_{C,P}$ = 8.3 Hz, *o*-Ph), 127.2 (d, $^3J_{C,P}$ = 7.2 Hz, *o*-Ph), 128.3 (s, Ph), 128.6 (s, Ph), 129.4 (d, $^2J_{C,P}$ = 16.2 Hz, *i*-Ph), 129.5 (d, $^2J_{C,P}$ = 14.4 Hz, *i*-Ph), 130.1 (s, Ph), 131.2 (s, Ph), 138.3 (d, $^1J_{C,P}$ = 57.5 Hz, C-3′), 141.4 (dd, $^1J_{C,P}$ = 28.3 Hz, $^2J_{C,P}$ = 4.0 Hz, C-3), 213.7 (d, $^2J_{C,P}$ = 18.0 Hz, CO); *minor diastereomer*: δ = 34.2 (s, CH_2-CH_3), 35.8 [s, $C(CH_3)_2$Et], 125.0 (d, $^1J_{C,P}$ = 21.5 Hz, C-2), 128.3 (s, Ph), 128.6 (s, Ph), 130.0 (s, Ph), 130.9 (s, Ph), 134.8 (d, $^1J_{C,P}$ = 59.2 Hz, C-3′), 139.9 (d, $^1J_{C,P}$ = 27.8 Hz, C-3), 214.1 (d, $^2J_{C,P}$ = 18.0 Hz, CO). − MS (EI, 70 eV): *m*/*z* (%) = 574 (1) [M^+], 462 (7) [M^+ − 4CO], 172 (28) [$C_{13}H_{16}^+$], 157 (14) [$C_{12}H_{13}^+$], 143 (100) [$C_{11}H_{11}^+$], 128 (23) [$C_{10}H_8^+$]. − HR-MS (EI, 70 eV); [M^+]: calcd. 574.1135; found 574.1130.

Synthesis of the (1,1′-Bi-1*H*-phosphirene)diiron Complexes 9a, b. − General Procedure: A mixture of the diastereomers of the corresponding mono complexed 1,1′-bi-1*H*-phosphirenes **7** was dissolved in *n*-pentane and treated with an excess of nonacarbonyldiiron. The suspension was stirred at room temp. for 24 h. The resulting dark red reaction solvents were evaporated to dryness. The brown residue was purified by column chromatography on neutral aluminum oxide with *n*-pentane as eluent. Recrystallization from *n*-pentane gave products **9a** and 9**b** as yellow crystals.

[μ-[3,3′-Bis(1,1-dimethylethyl)-2,2′-diphenyl-1*H*-phosphirene-κ*P*¹:κ*P*¹′]]octacarbonyldiiron (9a): Starting materials: 404 mg (0.74 mmol) **7a**, 538 mg (1.48 mmol) nonacarbonyldiiron. − Yield 330 mg (63%), yellow crystals, mixture of two diastereomers (ratio 10:1). − m.p.: 135 °C (decomposition). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2968 (m), 2930 (w), 2060 (s, CO), 2044 (s, CO), 1948 (vs, CO), 1938 (vs), 1098 (w), 1026 (w), 798 (w), 622 (m), 610 (m). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): *major diastereomer*: δ = −69.3 (s); *minor diastereomer*: δ = −66.8 (s). − ^1H NMR ($CDCl_3$): *major diastereomer*: δ = 1.52 [s, 18 H, $C(CH_3)_3$]; *minor diastereomer*: δ = 1.49 [s, 18 H, $C(CH_3)_3$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): not all signals could be assigned because of overlapping effects: *major diastereomer:* δ = 29.3 [pseudo-t, $|^3J_{C,P} + {}^4J_{C,P}|$ = 4.2 Hz, $C(CH_3)_3$], 34.8 [pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 3.4 Hz, $C(CH_3)_3$], 126.1 (pseudo-t, $|^3J_{C,P} + {}^4J_{C,P}|$ = 3.4 Hz, *o*-Ph), 128.5 (pseudo-t, $|^1J_{C,P} + {}^2J_{C,P}|$ = 15.2 Hz, C-2−C-2′), 128.9 (s, *m*-Ph), 130.4 (pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 5.9 Hz, *i*-Ph), 130.6 (d, $^5J_{C,P}$ = 1.7 Hz, *p*-Ph), 142.2 (pseudo-t, $|^1J_{C,P} + {}^2J_{C,P}|$ = 22.0 Hz, C-3−C-3′), 213.1 (pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 17.0 Hz, CO); *minor diastereomer*: δ = 29.7 [pseudo-t, $|^3J_{C,P} + {}^4J_{C,P}|$ = 5.0 Hz, $C(CH_3)_3$], 34.7 [pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 3.4 Hz, $C(CH_3)_3$], 126.0 (pseudo-t, $|^3J_{C,P} + {}^4J_{C,P}|$ = 3.4 Hz, *o*-Ph), 142.3 (pseudo-t, $|^1J_{C,P} + {}^2J_{C,P}|$ = 20.4 Hz, C-3−C-3′), 213.2 (pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 17.8 Hz, CO). − MS (EI, 70 eV): *m*/*z* (%) = 714 (0.02) [M^+], 490 (72) [M^+ − 8CO], 434 (14) [M^+ − Fe − 8CO], 332 (100) [M^+ − 8CO − $C_{12}H_{14}$], 287 (24) [M^+ − 8CO − $C_{12}H_{14}$ − $3CH_3$], 276 (49) [M^+ − Fe − 8CO − $C_{12}H_{14}$], 158 (36) [$C_{12}H_{14}^+$], 143 (96) [$C_{11}H_{11}^+$]. − $C_{32}H_{28}Fe_2P_2O_8$ (714.21 g/mol): calcd. C 53.82, H 3.95; found C 53.12, H 4.20.

μ-[3,3′-Bis(1,1-dimethylpropyl)-2,2′-diphenyl-1*H*-phosphirene-κ*P*¹:κ*P*¹′]octacarbonyldiiron (9b): Starting materials: 471 mg (0.82 mmol) **7b**, 597 mg (1.64 mmol) nonacarbonyldiiron. − Yield 330 mg (54%), mixture of two diastereomers (ratio 6:1). − IR (KBr, cm^{-1}): nu(tide) = 2970 (w), 2044 (s, CO), 1982 (m, CO), 1936 (vs, CO), 1468 (w), 1444 (w), 760 (m). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): *major diastereomer*: δ = −70.5 (s); *minor diastereomer*: δ = −67.4 (s). − ^1H NMR ($CDCl_3$): *major diastereomer*: δ = 0.90 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_2-CH_3), 1.42, 1.45 [each s, 12 H, $C(CH_3)_2CH_2$], 1.80 (q, $^3J_{H,H}$ = 7.2 Hz, 4 H, CH_2-CH_3); *minor diastereomer*: the signals could not be assigned because of overlapping effects and low intensity signals. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): *major diastereomer:* δ = 8.8 (d, $^4J_{C,P}$ = 8.8 Hz, CH_2-CH_3), 26.0 [s, $C(CH_3)_2$Et], 26.2 [s, $C(CH_3)_2$Et], 34.2 (d, $^3J_{C,P}$ = 10.4 Hz, CH_2-CH_3), 38.3 [d, $^2J_{C,P}$ = 14.5 Hz, $C(CH_3)_2$Et], 126.3 (d, $^1J_{C,P}$ = 20.0 Hz, C-2−C-2′), 128.9 (s, *m*-Ph), 129.9 (pseudo-t, $|^2J_{C,P} + {}^3J_{C,P}|$ = 7.2 Hz, *i*-Ph), 130.4 (d, $^3J_{C,P}$ = 6.4 Hz, *o*-Ph), 130.5 (d, $^5J_{C,P}$ = 3.2 Hz, *p*-Ph), 141.6 (pseudo-t, $|^1J_{C,P} + {}^2J_{C,P}|$ = 12.0 Hz, C-3−C-3′), 213.7 (d, $^2J_{C,P}$ = 4.8 Hz, CO); *minor diastereomer*: the signals could not be assigned because of overlapping effects and low intensity signals. − MS (EI, 70 eV): *m*/*z* (%) = 742 (0.04) [M^+], 518 (24) [M^+ − 8CO], 346 (38) [M^+ − 8CO − $C_{13}H_{16}$], 290 (29) [M^+ − Fe − 8CO − $C_{13}H_{16}$], 143 (100) [$C_{11}H_{11}^+$], 128 (20) [$C_{10}H_8^+$]. − $C_{34}H_{32}Fe_2P_2O_8$ (742.26 g/mol): calcd. C 55.02, H 4.35; found C 53.95, H 4.10.

Photolysis of the (1,1′-Bi-1*H*-phosphirene)diiron Complexes 9a and 9b. − General Procedure: A solution of **9a** or **9b** in C_6D_6 (1 − 2 mL) was irradiated with a high-pressure mercury lamp (λ ≤ 280 nm) and the reaction was monitored by ^{31}P NMR spectroscopy (7 − 9 h). After evaporation of the solvent under vacuum the residue was purified by column chromatography on neutral aluminum oxide with *n*-pentane/diethyl ether (1:1) as eluent. Recrystallization from *n*-pentane/diethyl ether (1:1) gave **10a** and **10b** as red crystals.

Hexacarbonyl-μ-[η¹:η³-{1-[2′-(1,1-Dimethylethyl)-3′-phenyl-1′-phosphapropenyl-κ*P*¹′:κ*C*²′:κ*C*³′]-3-(1,1-dimethylethyl)-2-phenyl-1*H*-phosphirene-κ*P*¹}]diiron(*Fe*−*Fe*) (10a): Starting material: 471 mg (0.66 mmol) (**9a**). − Yield 20 mg (5%), red crystals. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −1.6 (d, $^1J_{P,P}$ = 312.2 Hz, P-1′), −70.4 (d, $^1J_{P,P}$ = 312.2 Hz, P-1). − ^1H NMR ($CDCl_3$): δ = 1.16, 1.42 [each s, 18 H, $C(CH_3)_3$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.7 [d, $^3J_{C,P}$ = 2.6 Hz, $C(CH_3)_3$], 34.1 [d, $^3J_{C,P}$ = 2.6 Hz, $C(CH_3)_3$], 34.5 [d, $^2J_{C,P}$ = 5.1 Hz, $C(CH_3)_3$], 41.0 [dd, $^2J_{C,P}$ = 16.1 Hz, $^3J_{C,P}$ = 1.7 Hz, $C(CH_3)_3$], 124.6 (d, $^1J_{C,P}$ = 16.9 Hz, C-2), 126.6 (s, Ph), 127.1 (d, $J_{C,P}$ = 6.8 Hz, Ph), 127.6 (s, Ph), 129.1 (s, Ph), 130.0 (s, Ph), 130.5 (s, Ph), 130.9 (d, $J_{C,P}$ = 5.1 Hz, Ph), 134.2 (s, Ph), 134.5 (s, Ph), 150.6 (d, $^1J_{C,P}$ = 41.5 Hz, C-3), 153.9 (d, $^2J_{C,P}$ = 2.5 Hz, C-3′), 191.2 (dd, $^1J_{C,P}$ = 11.0 Hz, $^2J_{C,P}$ = 5.1 Hz, C-2′), 205.4 [d, $^2J_{C,P}$ = 27.6 Hz, $Fe(CO)_3$], 209.2 [d, $^2J_{C,P}$ = 27.1 Hz, $Fe(CO)_3$], 211.4 [d, $^2J_{C,P}$ = 28.8 Hz, $Fe(CO)_3$], 212.4 [d, $^2J_{C,P}$ = 6.8 Hz, $Fe(CO)_3$]. − MS (EI, 70 eV): *m/z* (%) = 658 (0.06) [M^+], 490 (20) [M^+ − 6CO], 332 (34) [M^+ − 6CO − $C_{12}H_{14}$], 158 (80) [$C_{12}H_{14}^+$], 143 (100) [$C_{11}H_{11}^+$], 128 (31) [$C_{10}H_8^+$]. − $C_{30}H_{28}Fe_2P_2O_6$ (658.187 g/mol): calcd. C 54.75, H 4.29; found C 54.49, H 4.31.

Hexacarbonyl-μ-[η¹:η³-{1-[2′-(1,1-Dimethylpropyl)-3′-phenyl-1′-phosphapropenyl-κ*P*¹′:κ*C*²′:κ*C*³′]-3-(1,1-dimethylpropyl)-2-phenyl-1*H*-phosphirene-κ*P*¹}]diiron(*Fe*−*Fe*) (10b): Starting material: 401 mg (0.54 mmol) **9b**. − Yield 20 mg (6%), red crystals. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 4.2 (d, $^1J_{P,P}$ = 315.2 Hz, P-1′), −69.5 (d, $^1J_{P,P}$ = 315.2 Hz, P-1). − ^1H NMR ($CDCl_3$): δ = 0.80 − 1.02 (m, 6 H, $CH_2{-}CH_3$), 1.17 [s, 3 H, $C(CH_3)_2CH_2$], 1.38 [s, 9 H, $C(CH_3)_2CH_2$], 1.74 (m, 4 H, $CH_2{-}CH_3$). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.7 (s, CH_2-CH_3), 10.1 (s, CH_2-CH_3), 27.2 [d, $^3J_{C,P}$ = 2.5 Hz, $C(CH_3)_2Et$], 27.3 [d, $^3J_{C,P}$ = 2.5 Hz, $C(CH_3)_2Et$], 31.8 [s, $C(CH_3)_2Et$], 34.8 (d, $^3J_{C,P}$ = 1.7 Hz, $CH_2{-}CH_3$), 37.7 (d, $^3J_{C,P}$ = 0.9 Hz, $CH_2{-}CH_3$), 38.3 [d, $^2J_{C,P}$ = 4.2 Hz, $C(CH_3)_2Et$], 43.8 [d, $^2J_{C,P}$ = 14.4 Hz, $C(CH_3)_2Et$], 124.6 (d, $^1J_{C,P}$ = 18.7 Hz, C-2), 126.1 (s, Ph), 126.7 (s, Ph), 128.2 (s, Ph), 128.4 (s, Ph), 128.7 (s, Ph), 129.0 (s, Ph), 129.1 (s, Ph), 129.4 (s, Ph), 130.1 (d, $J_{C,P}$ = 21.2 Hz, Ph), 130.7 (d, $J_{C,P}$ = 4.2 Hz, Ph), 150.4 (d, $^1J_{C,P}$ = 44.1 Hz, C-3), 153.8 (d, $^2J_{C,P}$ = 0.9 Hz, C-3′), 192.9 (dd, $^1J_{C,P}$ = 17.0 Hz, $^2J_{C,P}$ = 7.6 Hz, C-2′), 205.0 [d, $^2J_{C,P}$ = 30.6 Hz, $Fe(CO)_3$], 205.6 [d, $^2J_{C,P}$ = 27.1 Hz, $Fe(CO)_3$], 209.3 [d, $^2J_{C,P}$ = 25.4 Hz, $Fe(CO)_3$], 212.5 [d, $^2J_{C,P}$ = 5.1 Hz, $Fe(CO)_3$]. − MS (EI, 70 eV): *m/z* (%) = 686 (0.4) [M^+], 346 (18) [M^+ − 6 CO − $C_{13}H_{16}$], 172 (25) [$C_{13}H_{16}^+$], 143 (100) [$C_{11}H_{11}^+$], 128 (23) [$C_{10}H_8^+$].

Crystallographic Data for 10a: Crystallization of **10a** from different solvents and inspection of the crystals by preliminary X-ray crystallographic studies, showed that all investigated specimens were twinned. The twinning element was in all cases a twofold axis along [100]. According to the metrical peculiarity of the monoclinic lattice constants [a = 14.045(1), b = 11.127(1), c = 20.109(2) Å, β = 99.077(10)°, V = 3103.3(5) Å³, Z = 4] all reflections *hkl* with h = 0, 9, 11, −9, −11 overlap nearly exactly, while the reflections of all other layers, depending on the resolution of the diffractometer setting, are more or less separated (twinning by reticular meohedry). The twin matrix evaluated from the orientation matrices of both twin components was calculated to (1 0 0, 0 −1 0, −0.4526 0 −1). Data collection on an IPDS-diffractometer has been performed using a light yellow crystal with the dimensions 0.30 × 0.25 × 0.20 mm³.

The standard integration and data reduction methods[20] results in data sets, that only contain non-overlapped reflections. Structure solution by direct methods and completion of the structure model by difference Fourier synthesis using only these non-overlapping reflections succeeded in the space group $P2_1/n$. For a twin refinement in SHELXL-97[21] by the method of Pratt, Coyle, and Ibers[22] for the overlapped reflections the sum of F_c^2 values of the individual twin components, each multiplied by its fraction contribution, was fitted to the F_o^2 value and its fraction contribution. Hence, the diffractometer output has to be reformatted according to the above-mentioned twin law, and all reflections that neither overlap exactly nor can be resolved properly have been discarded. A simultaneous refinement of both twin components converged to a twin ratio of 0.3957/0.6043(5). All hydrogen atoms were included in the last stages of refinement in geometrically calculated positions, and their U_{iso} values were set to 1.2 and 1.5 times the U_{eq} value of the corresponding aromatic and methyl carbon atoms, respectively. Refinement of 410 parameters based on 9292 reflections converged to $wR2(F^2)$ = 0.0781, R1(F) = 0.0353 [for 6237 reflections with $F_o^2 > 2\sigma(F_o^2)$], GoF = 1.029, $\Delta\rho_{min}/\Delta\rho_{max}$ = −0.198/0.231 e/Å³, $(\Delta/\sigma)_{max}$ = 0.045.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157268. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] C. Peters, S. Stutzmann, H. Disteldorf, S. Werner, U. Bergsträßer, C. Krüger, P. Binger, M. Regitz, *Synthesis* **2000**, 529.

[2] M. Regitz, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, (Eds. M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 77−83.

[3] G. Märkl, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, (Eds. M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 220−249.

[4] J. Fink, W. Rösch, U.-J. Vogelbacher, M. Regitz, *Angew. Chem.* **1986**, *98*, 265−266; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 280−282.

[5] K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink, M. Regitz, *Angew. Chem.* **1987**, *99*, 67−68; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 85−86.

[6] [6a] D. Böhm, F. Knoch, S. Kummer, U. Schmidt, U. Zenneck, *Angew. Chem.* **1995**, *107*, 251−254; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 198−201. − [6b] N. Avarvari, L. Ricard, F. Mathey, P. Le Floch, O. Löber, M. Regitz, *Eur. J. Org. Chem.* **1998**, 2039−2045. − [6c] M. Hofmann, H. Heydt, M. Regitz, *Synthesis* **2001**, 463−467.

[7] [7a] G. Märkl, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, (Eds. M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 252−253. − [7b] Y. Kobayashi, I. Kumadaki,

A. Ohsawa, H. Hamana, *Tetrahedron Lett.* **1976**, 3715–3716. [7c] Y. Kobayashi, H. Hamana, S. Fujino, A. Ohsawa, I. Kumadaki, *J. Am. Chem. Soc.* **1980**, *102*, 252–255.

[8] [8a] A. Mack, F. Tabellion, C. Peters, A. Nachbauer, U. Bergsträßer, F. Preuss, M. Regitz, *Phosphorus, Sulfur and Silicon* **1999**, *144/146*, 261–264. [8b] A. Mack, M. Regitz, in: *Advances in Strained and Interesting Organic Molecules* (Ed.: B. Halton), Suppl. 1, JAI Press Inc., Cambridge, Conn., **1999**, p. 199–221.

[9] Short communication: J. Simon, U. Bergsträßer, M. Regitz, *Chem. Commun.* **1998**, 867–868.

[10] Y. Kabe, K. Ohkubo, H. Ishikawa, W. Ando, *J. Am. Chem. Soc.* **2000**, *122*, 3775–3776.

[11] A. Marinetti, F. Mathey, J. Fischler, A. Mitschler, *J. Chem. Soc., Chem. Commun.* **1984**, 45–46.

[12] [12a] H. Heydt, in: *Science of Synthesis, Vol. 9* (Eds. G. Maas, M. Regitz), Thieme, Stuttgart, **2000**, p. 85–124. – [12b] F. Mathey, M. Regitz, in: *Comprehensive Heterocyclic Chemistry II, Vol. 1A* (Eds. A. R. Katritzky, C. W. Rees), Pergamon, Oxford, **1996**, p. 227–304. – [12c]F. Mathey, *Chem. Rev.* **1990**, *90*, 997–1025.

[13] [13a] O. Wagner, M. Ehle, M. Regitz, *Angew. Chem.* **1989**, *101*, 227–229; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 225–226. – [13b] O. Wagner, M. Ehle, M. Birkel, J. Hoffmann, M. Regitz, *Chem. Ber.* **1991**, *124*, 1207–1213. – [13c] H. Heydt, M. Ehle, S. Haber, J. Hoffmann, O. Wagner, A. Göller, T. Clark, M. Regitz, *Chem. Ber./Recueil* **1997**, *130*, 711–723.

[14] A. Marinetti, F. Mathey, *J. Am. Chem. Soc.* **1985**, *107*, 4700–4706.

[15] [15a] K. Knoll, O. Orama, G. Huttner, *Angew. Chem.* **1984**, *96*, 989; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 976. –[15b] K. Knoll, G. Huttner, T. Fässler, L. Zsolnai, *J. Organomet. Chem.* **1987**, *327*, 255–267.

[16] [16a] C. E. Sumner, Jr., J. A. Collier, R. Petitt, *Organometallics* **1982**, *1*, 1350–1360. – [16b] T. E. Snead, C. A. Mirkin, K.-L. Lu, H. L. Beckman, G. L. Geoffroy, *Organometallics* **1992**, *11*, 942–954.

[17] [17a] F. W. B. Einstein, R. D. G. Jones, *J. Chem. Soc., Dalton Trans.* **1972**, 442–446. – [17b] R. E. Riley, R. E. Davis, *Inorg. Chem.* **1980**, *19*, 159–165. – [17c] R. L. Keiter, A. L. Rheingold, J. J. Hamerski, C. K. Castle, *Organometallics* **1983**, *2*, 1635–1639.

[18] D. G. Gilheany, in: *The Chemistry of Organophosphorus Compounds, Vol. 1* (Eds. S. Patai, F. R. Hartley), Wiley, Chichester, **1990**, p. 9–50.

[19] F. A. Ajulu, D. Carmichael, P. B. Hitchcock, F. Mathey, M. F. Meidine, J. F. Nixon, L. Ricard, M. L. Riley, *J. Chem. Soc., Chem. Commun.* **1992**, 750–752.

[20] Stoe & Cie., *IPDS-Software*, Vers. 2.87, Stoe & Cie. GmbH, Darmstadt, **1998**.

[21] G. M. Sheldrick, *SHELXL-97*, Program for the refinement of crystal structure, Universität Göttingen, **1997**.

[22] [22a] C. N. Pratt, B. A. Coyle, J. A. Ibers, *J. Chem. Soc. (A)* **1971**, 2146–2151. [22b] G. B. Jameson, *Acta Crystallogr., Sect. A* **1982**, *38*, 817–820.

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