Strained, Stable 2-Aza-1-Phosphabicyclo[*n*.1.0]alkane and -alkene $Fe(CO)_4$ Complexes with Dynamic Phosphinidene Behavior

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Abstract: The synthesis of highly strained bicyclic phosphirane and phosphirene iron–tetracarbonyl complexes, that is, complexes with 2-aza-1-phosphabicyclo[*n*.1.0]alkanes and -alkenes ($n=3$–5), is explored by using intramolecular cycloaddition of an in situ generated electrophilic phosphinidene complex, [R(*i*Pr)NP=$Fe(CO)_4$], to its C=C- and C≡C-containing R substituent. Saturated bicyclic complexes **7a–c** with $n=4$–2 are remarkably stable, as illustrated by the X-ray crystal structure for **7b** ($n=3$), yet all readily undergo retroaddition to react with phenylacetylene. Shuttling of the phosphinidene iron complex between two equivalent C=C groups is demonstrated for a 1-butene-substituted 2-aza-1-phosphabicyclo[3.1.0]hexane by selective ^{1}H NMR magnetization transfer from the phosphirane protons to the olefinic protons. Even the more strained unsaturated bicycles **17a**,**b** ($n=4$,3) are surprisingly stable as illustrated by the X-ray crystal structure for **17a** ($n=4$), but the smaller phosphabicyclo-[3.1.0]hex-5-ene (**17c**, $n=2$) dimerizes to tricyclic **19** with a unique ten-membered heterocyclic ring; an X-ray crystal structure is reported. Like their saturated analogues also the bicyclic phosphirenes readily undergo retroaddition as shown by the reaction of their phosphinidene iron moiety with phenylacetylene.

Keywords: iron · phosphinidenes · phosphorus heterocycles · small ring systems

Phosphinidenes (R–P), the phosphorus analogues of carbenes,[1] are elusive species,[2] yet when coordinated to a transition metal group, [R–P=ML_n], they are remarkably versatile with a significant synthetic scope.[3] There are two types, transient electrophilic or Fischer-type terminal phosphinidene complexes and those that are much more stable and nucleophilic or Schrock-type.[4] The electrophilic ones, particularly [R–P=$W(CO)_5$] (**1**), give access to many different heterocycles through addition to unsaturated bonds.[3] Cheletropic elimination from complexed 7-phosphanorbornadienes (**2**) is the most popular route to **1**,[5] but retroaddition from phosphiranes[6] or azaphosphirenes[7] (**3**) is also used occasionally (Scheme 1). Both routes are hampered by the tedious synthesis of the precursors. A much more convenient ionic path was recently reported by us for transient [iPr_2N–P=$Fe(CO)_4$] (**4**) that simply involves reacting Collman's reagent (**5**) with a dichlorophosphane (Scheme 1).[8] It was shown that this reagent is electrophilic as it adds to olefins and alkynes, but also that it appears less reactive than **1**, because the phosphiranes formed are thermally labile and easily give retroaddition.[9]

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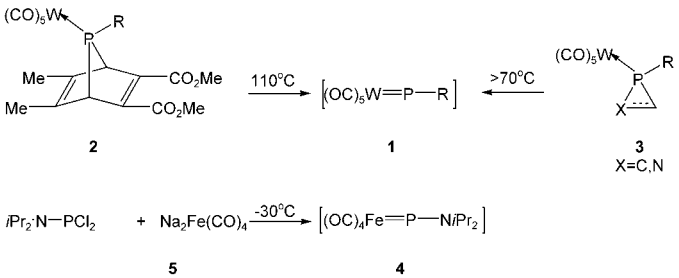

Scheme 1.

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In the present paper we expand on this ionic path and will show that stable bicyclic phosphiranes and phosphirenes can be formed by intramolecular cycloaddition of [R−P=$Fe(CO)_4$] to the double- or triple-bond-containing substituent R, respectively. Despite their stability, these bicyclic phosphorus heterocycles can undergo retroaddition, which will be illustrated by an intramolecular transfer of the carbene-like phosphinidene group.

Results and Discussion

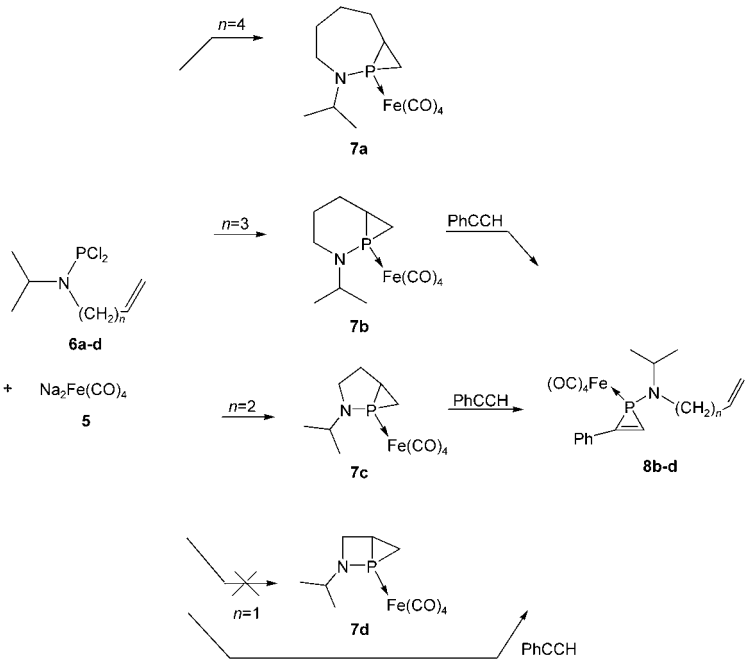
In the first part the formation and properties are described of differently sized bicyclic phosphiranes that result from the reaction of Collman's reagent with various dichloro aminophosphanes, of which the amino group carries a terminal olefinic group. As a special component a stable, but dynamic system will be presented in which the phosphinidene group transfers intramolecularly between olefinic groups. In the second part we address the intramolecular phosphinidene cycloaddition to triple bonds, instead of double bonds, to form the more strained, unsaturated bicyclic products. The synthesis of all starting materials is described in the Experimental Section.

Bicyclic phosphiranes: Reaction of $Na_2Fe(CO)_4$·1.5 dioxane (Collman's reagent) with dichloro(dialkylamino)phosphanes in diethyl ether or tetrahydrofuran at −30 °C results in the formation of various types of Fe/P clusters depending on the alkyl substituent and the reaction conditions.[10] Intermediate transient phosphinidene complex [iPr$_2$N−P=$Fe(CO)_4$] (**4**) can be isolated, both as a phosphirane[8a] and a phosphirene,[8b] showing that its affinity for terminal olefins and alkynes exceeds that for the self-condensation process. To examine the scope of this process we introduced additional ring strain by reacting the transient phosphinidene–iron complex intramolecularly with an olefinic group present in the amino substituent. We considered four cases in which the length n of the alkyl chain $(CH_2)_n$ that separates the olefin group from the amino nitrogen varies from 1 to 4. We started with the longest chain ($n=4$), as it presumably exerts the least strain on cyclization (Scheme 2).

After flash chromatography (−15 °C), reaction of **6a** with Collman's reagent in diethyl ether at −30 °C resulted in an orange oil (53 %) that consisted mainly (95 %) of the desired 2-aza-1-phosphabicyclo[5.1.0]octane **7a** accompanied by P,P-coupling products. The bicyclic structure is supported by a ^{31}P NMR resonance at $\delta=-41.3$ ppm that is typical for a $Fe(CO)_4$-complexed phosphirane,[8a] and by the different ^{1}H NMR resonances for the geminal methylene hydrogens of the three- and seven-membered rings. The conformational flexibility of **7a**, which is likely to occur through inversion at the nitrogen center, is illustrated by the splitting of its ^{31}P NMR resonance at $\delta=-41.3$ ppm into two signals of nearly equal intensity at $\delta=-34.5$ and -47.8 ppm at −78 °C. B3LYP/6–311+G(d,p) calculations[11] on model structures (labeled with capital letters, without $Fe(CO)_4$ and having a Me instead of an iPr substituent) support the existence of different diastereomers. A difference of 15.5 ppm in ^{31}P NMR chemical shifts is calculated for the lowest two energy structures of **7A** (Figure 1) that have a chair-and-boat conformation with the amino substituent in either an equatorial or axial position.

The balance between **7a** and the P,P-coupling products illustrates a marginal preference for cycloaddition of the transient phosphinidene–iron complex to the olefinic group over its self-condensation. The limited stability of **7a** hampered further purification and suggests that strain in the bicyclic structure may indeed be a limiting factor.

Reaction of Collman's reagent with **6b**, which has a shorter alkyl chain ($n=3$) for the olefinic substituent, surprisingly gives the tighter 2-aza-1-phosphabicyclo[4.1.0]heptane **7b** in a remarkably good isolated yield (63 %), as a stable yellow solid (m.p. 60–62 °C). X-ray single-crystal structure determination[12] confirmed the bicyclic structure of **7b** (Figure 2) and showed it to be in an axial position to the Fe complex, as expected for a weak π-acceptor ligand.[13] We are aware of only one other related crystal structure, namely that of the monocyclic 2,3,3-tri(trimethylsilyl)phosphirane–



Scheme 2. Synthesis and reactivity of bicyclic phosphiranes **7**.

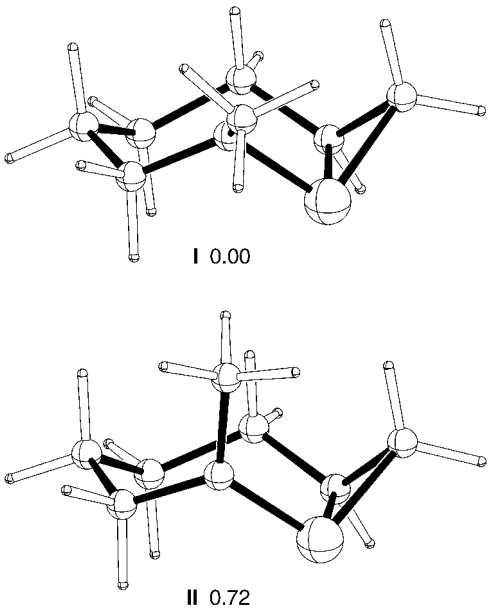


Figure 1. B3LYP/6–311+G(d,p) diastereomers and energies (in kcal mol^{-1}) of **7A** with equatorial (**I**) and axial (**II**) N-Me groups.

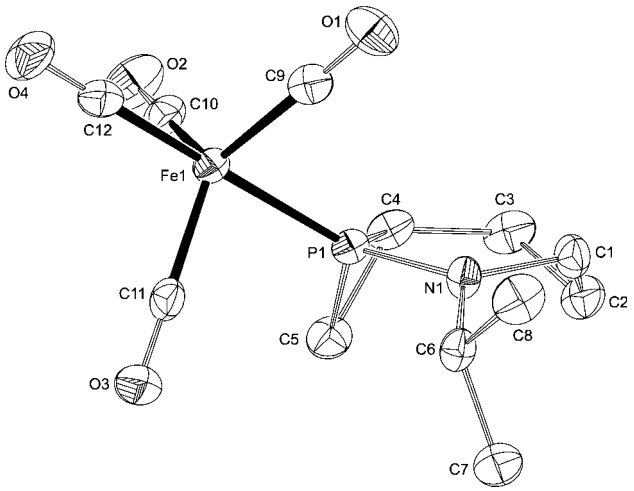
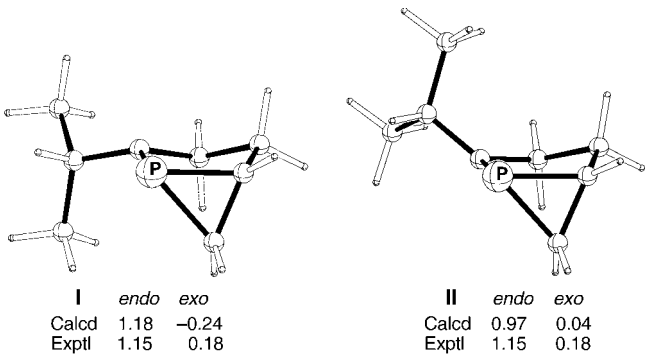


Figure 2. Displacement ellipsoid plot (50% probability level) of **7b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (deg) and torsion angles (deg): P1–Fe1 2.2222(5), P1–N1 1.6554(15), P1–C4 1.8053(18), P1–C5 1.8115(19), C4–C5 1.543(3), Fe1–C9 1.801(2), P1-C4-C5 64.95(10), P1-C5-C4 64.53(10), P1-Fe1-C9 88.15(6), Fe1-P1-N1 120.24(5), N1-P1-C4 106.06(8), N1-P1-C5 111.64(9), C4-P1-C5 50.52(9), C9-Fe1-P1-C5 −170.61(10), Fe1-P1-N1-C6 57.77(14), N1-P1-C4-C3 −6.26(18).

$Fe(CO)_2Cp$ complex.[14] The structural data of the C_2P ring of **7b** compare well with those of $W(CO)_5$-complexed phosphiranes.[15] For example, the P–C bond lengths of 1.8053(18) and 1.8115(19) Å are in the normal range (1.78–1.89 Å) as is the 50.52(9)° CPC angle (47.4–51.1°). Also the six-membered heterocyclic ring with its half-chair conformation appears to have normal P–N, C–N, and C–C bonds. Both the *i*Pr substituent and the metal fragment are oriented in the equatorial position. In solution, the observed ^{31}P NMR chemical shift at $\delta = -45.2$ ppm is very similar to that found for **7a**, but the more condensed structure of **7b** is evident from its more shielded ^{13}C NMR chemical shifts with differences of 6 and 8 ppm for those of the phosphirane ring. Also the ^{1}H NMR chemical shifts of particularly the *endo* and *exo* methylene hydrogen atoms of this ring are more shielded ($\delta = 0.87$ and 1.47 ppm) with a larger difference between them (**7b** $\Delta\delta_H = 0.61$, **7a** $\Delta\delta_H = 0.39$). The nearly exclusive formation of **7b** might suggest that the bicyclic structure is less strained than that of **7a**, and may be due to the preference of the phosphorus atom for smaller bond angles.

The even more condensed bicyclic structure, 2-aza-1-phosphabicyclo[3.1.0]hexane **7c**, was obtained as a yellow liquid in 64% isolated yield from reaction of Collman's reagent with **6c**, in which the double bond is separated from the nitrogen by a C_2H_4 unit. Its ^{31}P NMR chemical shift at −19 ppm is deshielded by more than 20 ppm from those of the larger bicyclic structures (**7a**,**b**) and reported iron-complexed aminophosphiranes.[8a,9] The ^{13}C NMR chemical shifts of the carbon atoms of the phosphirane ring are shielded with respect to those of **7b** ($\Delta\delta_C = 7.7$ and 2.8 ppm), as are its geminal methylene hydrogen atoms ($\Delta\delta_H = 0.33$ and ~0.7 ppm) with an even larger difference between them (**7c** $\Delta\delta_H \sim 0.96$, **7b** $\Delta\delta_H = 0.61$ ppm). The $\Delta\delta_H = 0.96$ ppm for the (*exo-endo*) methylene hydrogen atoms of the three-membered ring is also large relative to that of the structurally related 3,4-methano-2-pyrrolidine ($\Delta\delta_H = 0.41$ ppm).[16] B3LYP/6–311+G(d,p) calculations[11] on model structure **7C** (without $Fe(CO)_4$) revealed two minima with the *i*Pr group in either the equatorial (**I**) or axial (**II**) position ($\Delta E_{ax-eq} = 2.0$ kcal mol^{-1}) with calculated ^{1}H NMR chemical shifts that are similar to those observed (see Figure 3). Given the bulkiness of the $Fe(CO)_4$ group it is difficult to judge whether the equitorial or axial form of **7c** is preferred.



I	*endo*	*exo*
Calcd	1.18	−0.24
Exptl	1.15	0.18

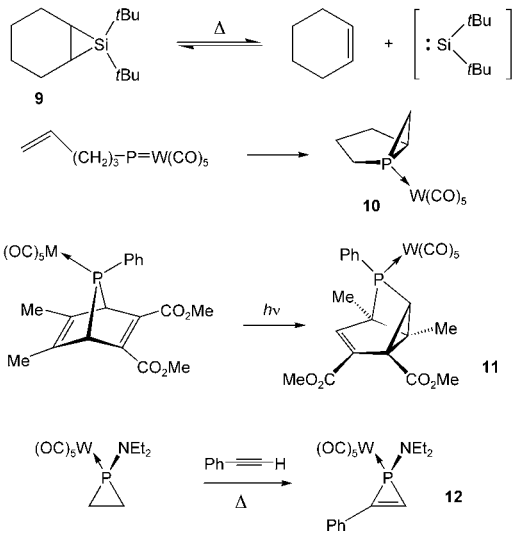
II	*endo*	*exo*
Calcd	0.97	0.04
Exptl	1.15	0.18

Figure 3. B3LYP/6–311+G(d,p) conformers of **7c** with calculated and observed ^{1}H NMR chemical shifts for the *endo* and *exo* phosphirane protons.

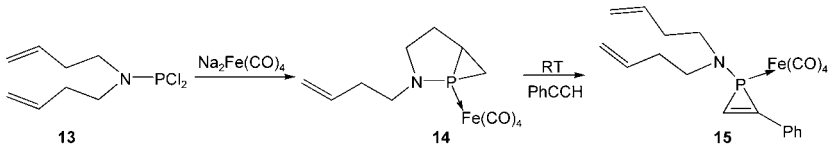
Attempts to synthesize 2-aza-1-phosphabicyclo[2.1.0]-pentane **7d** by intramolecular phosphinidene addition to the allylic group of **6d** failed. This bicyclic structure, containing

both four- and three-membered rings is apparently too strained to compete against the self condensation, as reaction of **6d** with Collman's reagent resulted only in a mixture of products that we assume to consist of Fe/P clusters as indicated by the ^{31}P NMR resonances ($\delta = 167$, -147 (J(P,P) = 275 Hz); $\delta = 145$, -137 (J(P,P) = 179 Hz)). Evidence for the intermediacy of a phosphinidene–iron complex was obtained by executing the reaction in the presence of one equivalent of phenylacetylene as trapping reagent. As expected, cycloadduct phosphirene **8d** was obtained in 56% isolated yield.

If bicyclic **7d** cannot be isolated, while the transient phosphinidene complex is trappable, and as the larger structure **7a** is of limited stability due to retroaddition and self-condensation to give Fe/P clusters, the question arises as to whether the remarkably stable bicyclic products **7b** and **7c** are also amenable to retroaddition. The fact that both these products undergo slow decomposition in solution would suggest such behavior. To clarify this we used phenylacetylene both as solvent and as a trapping reagent for the retroadduct (the phosphinidene–iron complex). Indeed, **7b** and **7c** are both converted in high (isolated) yield at room temperature to the corresponding phosphirenes **8b** (57%) and **8c** (76%). As determined by ^{31}P NMR spectroscopy, the reaction of **7b** with a k_{obs} of 3×10^{-4} s^{-1} is about 30 times faster than that of **7c**. This observation suggests that 2-aza-1-phosphabicyclo[3.1.0]hexane **7c** is the most stable bicyclic compound of the series.



Scheme 3.



Scheme 4.

Dynamic behaviour: In solution the bicyclic compounds undergo apparently rapid addition⇄retroaddition of [R*i*Pr-NPFe(CO)$_4$] to and from the double bond, a phenomenon so far only found for the reversible extrusion (>50 °C) of free silylenes from bicyclic silacyclopropanes **9** (Scheme 3).[17] In contrast, W(CO)$_5$-complexed phosphorus compounds are stable like **10**, which is also formed intramolecularly,[18] and **11**, which is formed photochemically from its phosphanorbornadiene precursor (Scheme 3).[19] Only at elevated temperatures (>50 °C) and in the presence of alkynes do the W(CO)$_5$-complexed amino-substituted phosphiranes convert into phosphirenes (for example, **12**, Scheme 3), although slow isomeric scrambling was observed for separate isomers of one such complex at room temperature.[6a]

The dynamic addition⇄retroaddition behavior of compounds **7a–c** would become even more evident if equivalent double bonds were to compete intramolecularly for the transient iron phosphinidene. To verify this we reacted symmetrically substituted **13** with Collman's reagent to synthesize **14** (71%) as a stable yellow liquid (Scheme 4). Not only are its ^{1}H, ^{13}C, and ^{31}P NMR characteristics for the bicyclic 2-aza-1-phosphabicyclo[3.1.0]hexane similar to those of **7c**, in phenylacetylene the $\delta = -19$ ppm ^{31}P NMR signal converts into one at $\delta = -37$ ppm, which is assigned to phosphirene **15**, thereby confirming the ability of **14** to undergo retroaddition.

The dynamic behavior of **14** with the phosphinidene–iron group exchanging between the double bonds can be shown spectroscopically. Of the various groups in the ^{1}H NMR spectrum (Figure 4a), the *endo* C*H*N ($\delta = 2.91$ ppm) and the *endo* C*H*P ($\delta = 1.23$ ppm) protons are readily identified by their NOE effect (Scheme 5, left-hand side). ^{1}H NMR NOE spectra at 74 °C in C_6D_6 reveal magnetization transfer between the two methylene hydrogen atoms of the phosphirane ring and the geminal hydrogen atoms of the olefinic group. Specifically, the *endo* C*H*P hydrogen atom ($\delta =$ 1.23 ppm) shows magnetization transfer with the olefinic hydrogen atom labeled H_c ($\delta = 4.98$ ppm) (Figure 4b) and the *exo* C*H*P hydrogen atom ($\delta = 0.24$ ppm) with olefinic hydrogen atom H_t ($\delta = 4.96$ ppm) (Figure 4c). These effects are best explained by shuttling of the transient phosphinidene complex between the two double bonds as illustrated in Scheme 5. Unfortunately, the exchange rate at 74 °C is too slow on the NMR timescale to acquire reliable kinetic data.

Bicyclic phosphirenes: The observed behavior of bicyclic phosphiranes **7a–d** results clearly from a balance between the energy gained by phosphinidene addition offset by the accompanying increase in strain. Phosphirenes have larger strain energies than phosphiranes, but phosphinidenes have a higher affinity for a triple bond than for a double bond, as

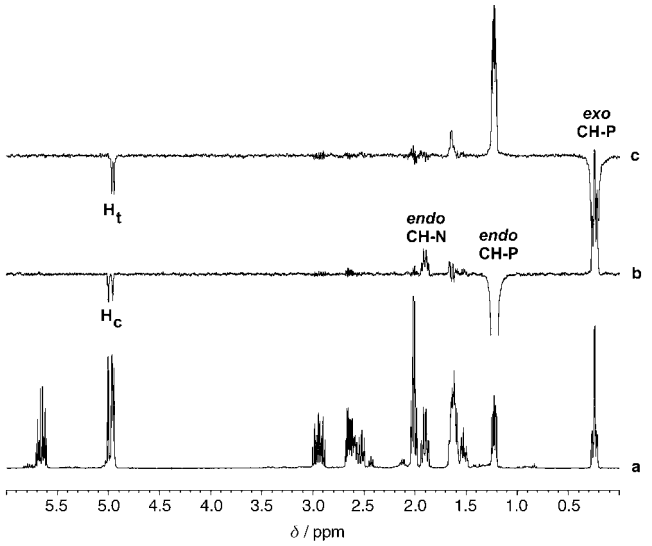
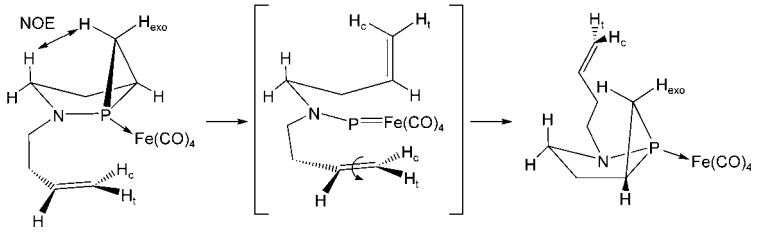


Figure 4. Proton spectra of a solution of **14** in C_6D_6 at 74 °C. a) the standard spectrum; b) and c) NOE spectra recorded after selective inversion of the signals at $\delta = 1.23$ ppm and $\delta = 0.24$ ppm, respectively, and a mixing time of 1.5 s. Negative signals around 5 ppm are due to chemical exchange. Positive signals are due to NOE.



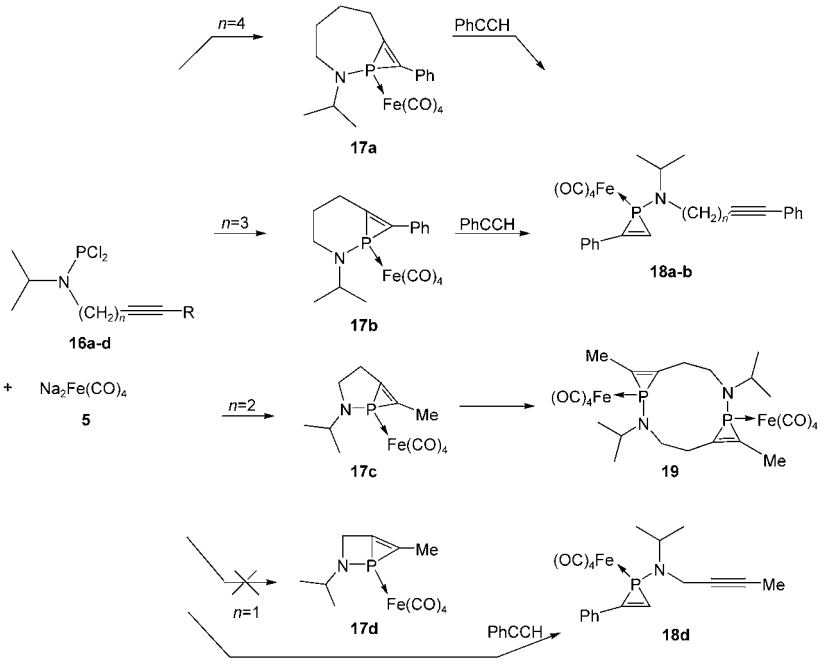
Scheme 5. Intramolecular phosphinidene exchange in **14**.

has been illustrated by their exchange. Hence, addition of $[R_2NPFe(CO)_4]$ to an internal triple bond may be expected to give similar dynamic phosphinidene behavior as discussed in the first section. Again, four cases are considered in which the length of alkyl chain $(-(CH_2)_n-)$ between the nitrogen and the triple bond varies with $n = 1$–4 (Scheme 6).

Starting with the longest chain ($n = 4$), reaction of **16a** with Collman's reagent gave in a remarkably good yield (60 %) the first bicyclic phosphirene, 2-aza-1-phosphabicyclo-[5.1.0]oct-7-ene **17a**, as a yellow solid (m.p. 71–72 °C). Its structure was confirmed with an X-ray single-crystal structure determination (Figure 5).[12] The geometrical features are as expected[8b] for a phosphirene with a CPC angle of 44.39(8)°, normal P–C bonds lengths (1.7522(18), 1.7810(17) Å), and a C=C bond (1.335(2) Å) conjugated with a phenyl ring (torsion angle −0.4(3)°). Also the ^{31}P NMR chemical shift in solution at $\delta = -42.3$ ppm is as expected, but the slightly shielded ^{13}C NMR resonances of the phosphirene carbons ($\delta \sim 7$ ppm) suggest some increased strain, as does the large $^1J(C,P)$ coupling constant for the phenyl-substituted carbon atom (37 Hz), being almost twice that found for other 2-phenylphosphirenes.[8b] In the crystal, the seven-membered ring adopts a twist-chair conformation[20] with the nitrogen atom deviating slightly from planarity (Σ angles 354.3°).

The ease of formation of **17a** is quite surprising. Presuming inherent ring strain to affect the stability of the phosphirene ring, we set out to examine whether **17a** was amenable to retroaddition, a process that has been observed for other 1-aminophosphirenes only above $T = 130$ °C,[6a] by attempting to trap the regenerated phosphinidene–iron complex intermolecularly with phenylacetylene that was also used as solvent. Gratifyingly, slow transfer was observed from **17a** ($\delta_P = -42$ ppm) to **18a** ($\delta_P = -37$ ppm) with an observed rate constant (k_{obs}) of 5×10^{-7} s^{-1} at room temperature.

Next we attempted the synthesis, under dilute conditions, of the still more strained bicyclic structure 2-aza-1-phosphabicyclo[4.1.0]hept-6-ene **17b** with an alkyl chain of $n = 3$. Monitoring the reaction of Collman's reagent with **16b** by ^{31}P NMR spectroscopy showed



Scheme 6. Synthesis and reactivity of bicyclic phosphiranes **17**.

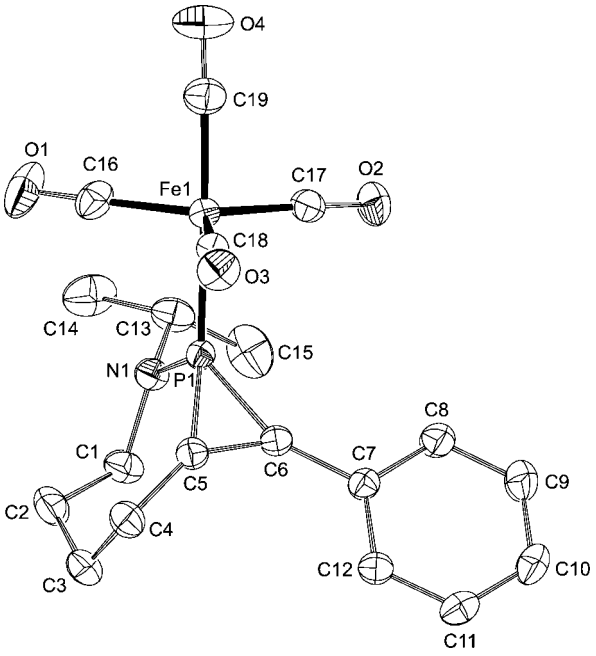


Figure 5. Displacement ellipsoid plot (50% probability level) of **17a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (deg) and torsion angles (deg): P1–Fe1 2.2244(5), P1–N1 1.6755(15), P1–C5 1.7522(18), P1–C6 1.7810(17), C5–C6 1.335(2), Fe1–C19 1.794(2), P1-C5-C6 68.95(11), P1-C6-C5 66.66(10), P1-Fe1-C18 90.26(6), Fe1-P1-N1 116.10(5), N1-P1-C5 107.09(8), C5-P1-C6 44.39(8), P1-C6-C7-C8 13.4(4), C5-C6-C7-C12 −0.4(3), Fe1-P1-N1-C1 −162.72(11), Fe1-P1-N1-C13 44.61(14).

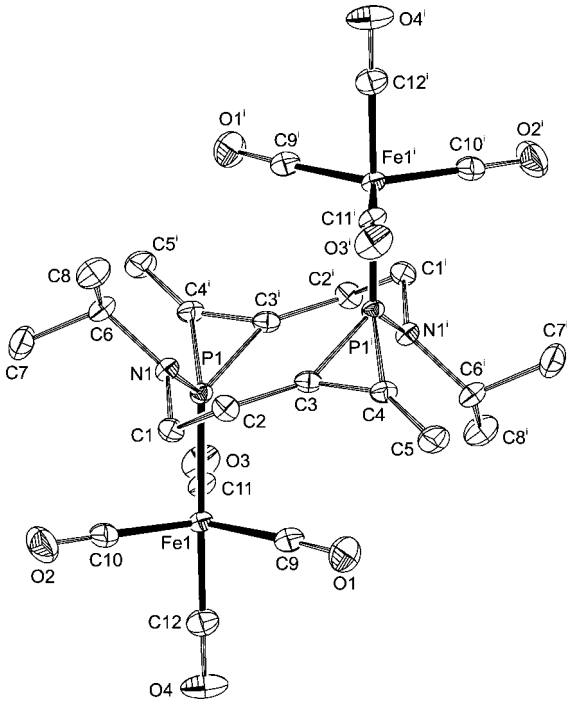


Figure 6. Displacement ellipsoid plot (50% probability level) of **19**. Hydrogen atoms are omitted for clarity. Symmetry operation i: $1-x$, $1-y$, $1-z$. Selected bond lengths (Å), angles (deg) and torsion angles (deg): P1–Fe1 2.2421(5), P1–N1 1.6841(14), P1–C3^{i} 1.7685(16), P1–C4^{i} 1.7591(16), C3–C4 1.325(2), Fe1–C12 1.7866(18), P1^{i}-C3-C4 67.55(10), P1^{i}-C4-C3 68.31(10), P1-Fe1-C11 85.98(5), Fe1-P1-N1 118.90(5), N1-P1-C3^{i} 114.82(7), C4^{i}-P1-C3^{i} 44.14(8), Fe1-P1-N1-C1 26.31(13), Fe1-P1-N1-C6 −124.80(10), C2-C3-C4-C5 4.8(4).

its quantitative formation ($\delta_P = -41$ ppm), but isolation as a pure substance proved to be tedious (28%, red-brown oil) due to slow decomposition and the formation of Fe/P clusters, indicating its limited stability. All NMR data support the assignment of structure **17b**, which has characteristic resonances for the phosphirene ring, but enhanced strain with respect to **17a** may be inferred from the larger ^{1}J(C,P) coupling constant (45 Hz) for the phenyl-substituted carbon atom. The much higher instability of this novel, highly strained bicyclic structure is further evident from its instantaneous reaction with phenylacetylene to give 2-phenylphosphirene **18c** ($\delta_P = -37$ ppm, 12% isolated yield) as well as Fe/P clusters.

It would appear that **17b** is the most strained bicyclic phosphirene feasible. Still, we pursued the viability of the even more strained **17c** by reacting Collman's reagent with phosphane **16c**, in which a C_2H_4 unit separates the nitrogen atom and the methyl-substituted acetylene. ^{31}P NMR spectroscopy showed the formation of related products (four resonances at $\delta = -33$ to -34.3 ppm), of which the major one ($\delta = -34.3$ ppm) could be isolated as a yellow solid (m.p. 124 °C) albeit in low yield (8%). An X-ray crystal structure determination[12] revealed this product (**19**) to be the unexpected dimer of bicyclic phosphirene **17c** (Figure 6). The tricyclic molecule is located on an inversion center in the crystal with a double-chair conformation for the unique ten-membered heterocyclic ring with the two *trans*-Fe(CO)$_4$ groups in axial positions. In the crystal, the phosphirene rings have typical bond lengths and angles and, in solution, normal ^{13}C chemical shifts for their carbon atoms ($\delta = 150$ and 153 ppm) and a coupling constant (^{1}J(C,P) = 19.4 Hz) for the methyl-substituted carbon atom comparable to other unsymmetrical 2-substituted phosphirenes (18–22 Hz).[8b] Surprising is the triplet for the methylene carbon atom (C2/C2^{i}), which apparently couples with both phosphorus atoms to the same extent (^{2}J(C,P) = ^{3}J(C,P) = 3.7 Hz).

The manner in which **19** is formed may be explained speculatively as follows. From **16c** an incipient phosphinidene–iron complex is generated, which may or may not be in equilibrium with **17c** by cycloaddition, and which than adds intermolecularly to the triple bond of another molecule of **16c**. Subsequent conversion of the PCl_2 group to a phosphinidene complex would then give **19** on ring-closure. This route would also explain the likely formation of byproducts other than the P/C-clusters, such as the *cis* isomer, and higher condensation products (trimers, etc.) in more concentrated solutions.

It is then not surprising that reaction of propargylic-substituted phosphane **16d** with Collman's reagent (**5**) did not result in a bicyclic product (**17d**) nor its dimer even in P/Fe clusters. However, because a phosphinidene iron complex is indeed generated in situ, as demonstrated by the formation 2-phenylphosphirene **18d** (26% yield) by performing the re-

action in the presence of phenylacetylene, we presume that polymerization takes place in the absence of a trapping reagent.

Conclusion

We have shown that, depending on the ring-size of the resulting bicyclic heterocycle, electrophilic phosphinidene [R*i*PrNP=Fe(CO)$_4$] can be trapped intramolecularly with double and triple bonds. The novel bicyclic 2-aza-1-phosphabicyclo[*n*.1.0]alkanes and -alkenes ($n=3$–5) show varying degrees of stability, and several could be isolated in a pure form. Remarkably, in all cases phosphinidene addition is reversible at room temperature, and in phenylacetylene phosphinidene exchange with solvent molecules was shown to take place. Generation of a bisbutenylaminophosphinidene–iron complex led to an olefinic-substituted phosphirane in which the phosphinidene exchange between the two double bonds was detected by means of dynamic NMR experiments at higher temperatures.

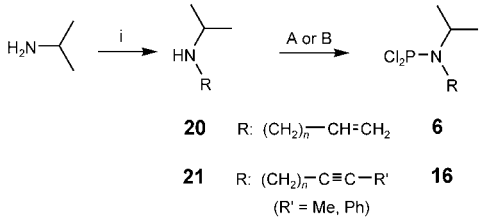
Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Isopropylamine and triethylamine were distilled and stored over KOH. PCl_3 was distilled prior to use. Solvents were distilled from $LiAlH_4$ (pentane, diethyl ether) or sodium benzophenone (THF). 1-Phenyl-6-bromo-1-hexyne,[21] 1-phenyl-5-bromo-1-pentyne,[22] 5-bromo-2-pentyne[23] and isopropyl-prop-2-enylamine[24] (**20d**) were synthesized according to literature methods. The secondary amines were synthesized according to the procedure of Surzur et al.[24] $Na_2Fe(CO)_4$·1.5 dioxane (Collman's reagent) was purchased from Fluka or synthesized according to literature procedures.[25] All other compounds were used as purchased.

NMR spectra were recorded at 25 °C (unless otherwise indicated) on Bruker AC 200 (^{1}H, ^{13}C), Bruker Avance 250 (^{1}H, ^{13}C, ^{31}P), and Bruker Avance 400 MHz (^{1}H, ^{13}C) spectrometers, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan MAT 900 spectrometer. NMR chemical shifts are internally referenced to the solvent for ^{1}H ($CDCl_3$: $\delta=7.25$ ppm, C_6D_6: $\delta=7.15$ ppm) and ^{13}C ($CDCl_3$: $\delta=77.0$ ppm, C_6D_6: $\delta=128$ ppm) and externally for ^{31}P to 85% H_3PO_4.

NOE spectra (Figure 4) were recorded with a double-pulsed field gradient spin-echo sequence (DPFGSE).[26]

General synthesis of the amines 20 and 21 (Scheme 7): The unsaturated group was introduced by alkylating isopropylamine (tenfold excess) with the appropriate unsaturated bromide at 50 °C in the dark. After removal of isopropylamine by distillation, the organic phase was treated with Et_2O and water, dried over Na_2SO_4, and concentrated. The crude product



Scheme 7.

(**20**, **21**) was used without further purification or distilled, depending on the purity.

Isopropylhex-5-enylamine (20a): Reaction time: 44.5 h; pale yellow liquid (91% yield); b.p. 170 °C/760 mm Hg; ^{13}C NMR ($CDCl_3$): $\delta=138.80$ (s, =CH), 114.42 (s, $=CH_2$), 48.70 (s, CHN), 47.46 (s, CH_2N), 33.67 (s, $CHCH_2$), 29.97 (s, CH_2CH_2N), 26.76 (s, $CH_2CH_2CH_2N$), 23.03 ppm (s, CH_3); ^{1}H NMR ($CDCl_3$,): $\delta=5.76$ (ddt, ^3J(H,H)(*trans*) = 17.0 Hz, ^3J(H,H)(*cis*) = 10.2 Hz, ^3J(H,H) = 6.8 Hz, 1H; =CH), 4.97 (m, 2H; $=CH_2$), 2.71 (septet, ^3J(H,H) = 6.3 Hz, 1H; CHN), 2.52 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2N), 2.00 (dt, ^3J(H,H) = 6.8 Hz, ^3J(H,H) = 7.1 Hz, 2H; CH_2–CH=), 1.39 (m, 4H; $-CH_2CH_2CH_2N$), 0.98 (d, ^3J(H,H) = 6.3 Hz, 6H; $(CH_3)_2CH$), 0.8–0.9 ppm (br, NH); IR (KBr): $\tilde{\nu}=3442.6$ (br), 2962.9 (m), 2928.1 (m), 1261.5 (s), 1099.5 (s), 1022.3 (s), 802.4 cm^{-1} (s); HRMS: *m*/*z* calcd for $C_9H_{19}N$: 141.15175; found: 141.15283; MS: *m*/*z* (%): 141 (6) [M^+], 140 (2) [M^+–H], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropylpent-4-enylamine (20b): Reaction time: 44 h; colorless liquid (96% yield); b.p. 70 °C/45 mm Hg; ^{13}C NMR ($CDCl_3$): $\delta=138.51$ (s, =CH), 114.54 (s, $=CH_2$), 48.67 (s, CHN), 47.00 (s, CH_2N), 31.66 (s, CH_2CH=), 29.61 (s, CH_2CH_2N), 23.03 ppm (s, $(CH_3)_2CH$); ^{1}H NMR ($CDCl_3$): $\delta=5.81$ (ddt, ^3J(H,H)(*trans*) = 17.0 Hz, ^3J(H,H)(*cis*) = 10.3 Hz, ^3J(H,H) = 6.6 Hz, 1H; =CH), 4.91–5.05 (m, 2H; $=CH_2$), 2.77 (septet, ^3J(H,H) = 6.2 Hz, 1H; CHN), 2.59 (t, ^3J(H,H) = 7.3 Hz, 2H; CH_2N), 2.04–2.13 (m, 2H; CH_2CH=), 1.51–1.63 (m, 2H; CH_2CH_2N), 1.03 (d, ^3J(H,H) = 6.2 Hz, 6H; $(CH_3)_2CH$), 0.8–1.0 ppm (br, NH); IR (KBr): $\tilde{\nu}=$ 3437.4 (w, br), 2962.9 (m), 2924.3 (m), 2852.9 (w), 1261.5 (s), 1099.5 (s), 1022.3 (s), 802.4 cm^{-1} (s); HRMS: *m*/*z* calcd for $C_8H_{17}N$: 127.13610; found: 127.13616; MS: *m*/*z* (%): 127 (1) [M^+], 126 (15) [M^+–H], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropylbut-3-enylamine (20c): Reaction time: 90 h; colorless liquid (72% yield); b.p. 131 °C (35 °C/42 mm Hg); ^{13}C NMR ($CDCl_3$): $\delta=136.59$ (s, =CH), 116.26 (s, $=CH_2$), 48.55 (s, CHN), 46.44 (s, CH_2N), 34.51 (s, $CHCH_2$), 22.96 ppm (s, $(CH_3)_2CH$); ^{1}H NMR ($CDCl_3$): $\delta=5.77$ (ddt, ^3J(H,H)(*trans*) = 17.2 Hz, ^3J(H,H)(*cis*) = 10.1 Hz, ^3J(H,H) = 6.9 Hz, 1H; =CH), 5.00–5.11 (m, 2H; $=CH_2$), 2.77 (septet, ^3J(H,H) = 6.2 Hz, 1H; NCH), 2.65 (t, ^3J(H,H) = 6.9 Hz, 2H; NCH_2), 2.23 (dt, ^3J(H,H) = ^3J(H,H) = 6.9 Hz, 2H; CH_2CH=), 1.04 (d, ^3J(H,H) = 6.2 Hz, 6H; CH_3), 0.8–1.0 ppm (br, 1H; NH); IR (KBr): $\tilde{\nu}=3447.0$ (s, br), 2959.0 (m), 2924.3 (s), 2852.9 (m), 1261.5 (m), 1101.4 (m), 1022.3 (m), 802.4 cm^{-1} (m); HRMS: *m*/*z* calcd for $C_7H_{15}N$: 113.12045; found: 113.11983; MS: *m*/*z* (%): 113 (1) [M^+], 112 (7) [M^+–H], 98 (8) [M^+–CH_3], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropyl(6-phenylhex-5-ynyl)amine (21a): Reaction time: 93 h; colorless liquid (64%); b.p. 55–60 °C/4 × 10^{-2} mm Hg; ^{13}C NMR ($CDCl_3$): $\delta=$ 131.53 (s, *o*-ArC), 128.15 (s, *m*-ArC), 127.49 (s, *p*-ArC), 123.99 (s, *ipso*-ArC), 90.02 (s, $CH_2C\equiv$), 80.80 (s, $\equiv CPh$), 48.72 (s, CHN), 47.13 (s, CH_2N), 29.80 (s, CH_2CH_2N), 26.71 (s, $CH_2CH_2C\equiv$), 23.06 (s, CH_3), 19.38 ppm (s, $CH_2C\equiv$); ^{1}H NMR ($CDCl_3$): $\delta=7.34$–7.40 (m, 2H; *o*-ArH), 7.23–7.28 (m, 3H; *m*,*p*-ArH), 2.79 (septet, ^3J(H,H) = 6.2 Hz, 1H; NCH), 2.63 (t, ^3J(H,H) = 6.2 Hz, 2H; CH_2N), 2.42 (t, ^3J(H,H) = 6.6 Hz, 2H; $CH_2C\equiv$), 1.60–1.68 (m, 4H; CH_2CH_2), 1.04 (d, ^3J(H,H) = 6.2 Hz, 6H; CH_3), 0.8–0.9 ppm (br, 1H; NH); IR (KBr): $\tilde{\nu}=3441.2$ (br), 2962.9 (s), 2933.9 (s), 2862.5 (m), 2231.8 (w), 1599.1 (w), 1491.1 (m), 1379.2 (m), 1331.8 (w), 1172.8 (m), 756.1 (s), 692.2 (s), 526.6 cm^{-1} (w); HRMS: *m*/*z* calcd for $C_{15}H_{21}N$: 215.16739; found: 215.16883; MS: *m*/*z* (%): 215 (<1) [M^+], 72 (76) [CH_2=N(H)*i*Pr$^+$], 43 (100) [$C_3H_7^+$].

Isopropyl(5-phenylpent-4-ynyl)amine (21b): Reaction time: 90 h; colorless liquid (79% yield); b.p. 70–80 °C/1–2 mm Hg; ^{13}C NMR ($CDCl_3$): $\delta=$ 131.52 (s, *o*-ArC), 128.18 (s, *m*-ArC), 127.54 (s, *p*-ArC), 123.95 (s, *ipso*-ArC), 89.72 (s, $CH_2C\equiv$), 80.92 (s, $\equiv CPh$), 48.63 (s, CHN), 46.51 (s, CH_2N), 29.32 (s, CH_2CH_2N), 23.07 (s, CH_3), 17.45 ppm (s, $CH_2C\equiv C$); ^{1}H NMR ($CDCl_3$): $\delta=7.36$–7.40 (m, 2H; *o*-ArH), 7.23–7.28 (m, 3H; *m*,*p*-ArH), 2.73–2.87 (m, 3H; $CHNCH_2$), 2.47 (t, ^3J(H,H) = 7.0 Hz, 2H; $CH_2C\equiv$), 1.77 (quintet, ^3J(H,H) = 7.0 Hz, 2H; CH_2CH_2N), 1.06 (d, ^3J(H,H) = 6.2 Hz, 6H; CH_3), 0.8–0.9 ppm (br, 1H; NH); IR (KBr): $\tilde{\nu}=$ 3435.4 (br), 2962.9 (m), 2361.0 (s), 2343.7 (s), 1489.1 (m), 756.1 (s), 692.5 cm^{-1} (s); HRMS: *m*/*z* calcd for $C_{14}H_{19}N$: 201.15175; found: 201.15254; MS: *m*/*z* (%): 201 (1) [M^+], 158 (100) [M^+–C_3H_7], 72 (76) [CH_2=N(H)*i*Pr$^+$].

Isopropylpent-3-ynylamine (21c): Reaction time: 90 h; colorless liquid (61% yield); b.p. 40–42 °C/42 mm Hg; ^{13}C NMR ($CDCl_3$): δ = 77.11 (≡*C*CH$_2$), 76.74 (Me−*C*≡), 48.13 (CHN), 46.10 (CH_2N), 22.97 (CH-(*C*H$_3$)$_2$), 20.05 ppm (*C*H$_2$C≡), 3.48 (*C*H$_3$C≡); ^{1}H NMR ($CDCl_3$): δ = 2.81 (septet, ^3J(H,H) = 6.2 Hz, 1H; CHN), 2.70 (t, ^3J(H,H) = 6.8 Hz, 2H; CH_2N), 2.27–2.35 (m, 2H; CH$_2$C≡), 1.77 (t, ^5J(H,H) = 2.5 Hz, 3H; CH$_3$C≡), 1.05 ppm (d, ^3J(H,H) = 6.2 Hz, 6H; (*C*H$_3$)$_2$CH); IR (KBr): $\tilde{\nu}$ = 3427.7 (br), 2966.7 (s), 2920.4 (m), 2843.3 (w), 1176.7 (w), 1086.0 (w), 1030.1 (w), 742.6 (br), 667.4 cm^{-1} (w); HRMS: *m*/*z* calcd for $C_8H_{15}N$: 125.12045; found: 125.12096; MS: *m*/*z* (%): 125 (2) [M^+], 110 (96) [M^+ −CH$_3$], 72 (100) [CH$_2$=N(H)*i*Pr$^+$].

Isopropylbut-2-ynylamine (21d): A slightly different approach was used. At 0 °C, 1-bromo-2-butyne (1.46 g, 11 mmol) was added dropwise with stirring to isopropylamine (8.0 mL, 110 mmol). A salt was formed after 1 min. Stirring was continued for 0.5 h at 0 °C, after which, the mixture was warmed to room temperature and worked up as usual, resulting in a colorless liquid (1.10 g, 9.9 mmol, 90% yield). B.p. 30–35 °C/50 mm Hg; ^{13}C NMR ($CDCl_3$): δ = 78.55 (s, ≡*C*CH$_2$), 77.43 (s, Me−*C*≡), 47.06 (s, CHN), 36.11 (s, CH_2), 22.56 ppm (s, (*C*H$_3$)$_2$CH), 3.47 (*C*H$_3$C≡); ^{1}H NMR ($CDCl_3$): δ = 3.35 (q, ^5J(H,H) = 2.4 Hz, 2H; CH_2), 2.96 (septet, ^3J(H,H) = 6.2 Hz, 1H; NCH), 1.79 (t, ^5J(H,H) = 2.4 Hz, 3H; CH$_3$C≡), 1.23 (br s, 1H; NH), 1.03 ppm (d, ^3J(H,H) = 6.2 Hz, 6H; (*C*H$_3$)$_2$CH); IR (KBr): $\tilde{\nu}$ = 3414.2 (br), 2966.7 (m), 2924.3 (m), 2856.8 (w), 1261.5 (m), 1101.42 (m), 1028.1 (m), 802.4 (m), 669.3 cm^{-1} (w); HRMS: *m*/*z* calcd for $C_7H_{13}N$: 111.10480; found: 111.10433; MS: *m*/*z* (%): 111 (<1) [M^+], 110 (5) [M^+−2H], 72 (100) [CH$_2$=N(H)*i*Pr$^+$].

General synthesis of the dichloroaminophosphanes 6, 13, and 16

Route A: *n*BuLi (1.6 M, hexane, 1 equiv) was added to a cold (−78 °C) solution of the amine (**20**, **21**) in Et$_2$O (15 mL mmol^{-1}). The reaction mixture was warmed to room temperature, and then it was added slowly to a cold (−78 °C) solution of PCl_3 (2 equiv) in Et$_2$O (15 mL mmol^{-1}). Warming of the reaction mixture to room temperature, filtration, solvent evaporation, and distillation gave the desired product (**6**, **16**) as an air- and light-sensitive liquid.

Route B: Et$_3$N (1 equiv) was added to a cold (−78 °C) solution of PCl_3 (1.3 equiv) in Et$_2$O (5 mL mmol^{-1}) after which the secondary amine (1 equiv) was added dropwise, resulting in the immediate formation of a white precipitate. The reaction mixture was stirred for an additional 30 min at −78 °C and for 3 h at room temperature and worked up to give the product (**6**, **13**, **16**) as air- and light-sensitive liquids.

Dichloro[isopropyl(hex-5-enyl)amino]phosphane (6a): Route B, 64% yield; b.p. 55–60 °C/1–2 mm Hg; ^{31}P NMR (C_6D_6): δ = 166.96 ppm; ^{13}C NMR (C_6D_6): δ = 138.44 (s, =CH), 114.97 (s, CH$_2$=), 51.54 (d, ^2J(C,P) = 22.9 Hz, CHN), 45.36 (d, ^2J(C,P) = 14.2 Hz, CH_2N), 33.52 (s, *C*H$_2$CH=), 30.62 (d, ^3J(C,P) = 5.6 Hz, *C*H$_2$CH$_2$N), 26.42 (s, *C*H$_2$CH$_2$C=), 22.32 ppm (d, ^3J(C,P) = 8.8 Hz, CH$_3$); ^{1}H NMR (C_6D_6): δ = 5.67 (ddt, ^3J(H,H)(*trans*) = 16.9 Hz, ^3J(H,H)(*cis*) = 10.3 Hz, ^3J(H,H) = 6.6 Hz, 1H; CH=), 4.93–5.01 (m, 2H; CH$_2$=), 3.49–3.57 (m, 1H; NCH), 2.82–2.93 (m, 2H; CH_2N), 1.81–1.89 (m, 2H; C*H*$_2$CH=), 1.30–1.40 (m, 2H; C*H*$_2$CH$_2$N), 1.06–1.18 (m, 2H; C*H*$_2$CH$_2$CH=), 0.88 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH$_3$); HRMS: *m*/*z* calcd for $C_9H_{18}NPCl_2$: 241.05539; found: 241.05435; MS: *m*/*z* (%): 241 (1) [M^+], 226 (12) [M^+−CH$_3$], 206 (26) [M^+−Cl], 172 (52) [H$_2$C=N(*i*Pr)NPCl$_2^+$].

Dichloro[isopropyl(pent-4-enyl)amino]phosphane (6b): Route A: 85% yield; b.p. 54 °C/1 mm Hg; ^{31}P NMR (C_6D_6): δ = 167.05 ppm; ^{13}C NMR (C_6D_6): δ = 137.85 (s, =CH), 115.56 (s, CH$_2$=), 51.79 (d, ^2J(C,P) = 23.1 Hz, NCH), 44.99 (d, ^2J(C,P) = 14.3 Hz, CH_2N), 31.30 (s, CH$_2$CH=), 30.34 (d, ^3J(C,P) = 5.6 Hz, *C*H$_2$CH$_2$N), 22.24 ppm (d, ^3J(C,P) = 8.7 Hz, (*C*H$_3$)$_2$CH); ^{1}H NMR (C_6D_6): δ = 5.61 (ddt, ^3J(H,H)(*trans*) = 16.9 Hz, ^3J(H,H)(*cis*) = 10.4 Hz, ^3J(H,H) = 6.6 Hz, 1H; =CH), 4.91–4.99 (m, 2H; CH$_2$=), 3.52 (dsp, ^3J(H,P) = 6.7 Hz, ^3J(H,H) = 6.8 Hz, 1H; NCH), 2.84–2.95 (m, 2H; CH_2N), 1.74–1.83 (m, 2H; C*H*$_2$CH=), 1.38–1.51 (m, 2H; C*H*$_2$CH$_2$N), 0.86 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; (C*H*$_3$)$_2$CH); HRMS: *m*/*z* calcd for $C_8H_{16}NPCl_2$: 227.03973; found: 227.04086; MS: *m*/*z* (%): 228 (3) [M^++H], 212 (12) [M^+−CH$_3$], 192 (100) [M^+−Cl], 172 (28) [H$_2$C=N(*i*Pr)NPCl$_2^+$].

Dichloro[isopropyl(but-3-enyl)amino]phosphane (6c): Route A: 87% yield; b.p. 50 °C/1 mm Hg; ^{31}P NMR (C_6D_6): δ = 166.70 ppm; ^{13}C NMR (C_6D_6): δ = 134.99 (s, =CH), 117.17 (s, CH$_2$=), 51.65 (d, ^2J(C,P) = 22.2 Hz, NCH), 44.90 (d, ^2J(C,P) = 13.9 Hz, CH_2N), 35.69 (d, ^3J(C,P) = 5.4 Hz, *C*H$_2$CH$_2$N), 22.21 ppm (d, ^3J(C,P) = 8.6 Hz, CH$_3$); ^{1}H NMR (C_6D_6): δ = 5.66 (ddt, ^3J(H,H)(*trans*) = 17.1 Hz, ^3J(H,H)(*cis*) = 10.3 Hz, ^3J(H,H) = 6.7 Hz, 1H; =CH), 4.89–4.97 (m, 2H; CH$_2$=), 3.45–3.61 (m, 1H; NCH), 2.90–3.01 (m, 2H; CH_2N), 2.05–2.14 (m, 2H; C*H*$_2$CH$_2$N), 0.86 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH$_3$); HRMS: *m*/*z* calcd for $C_7H_{14}NPCl_2$: 213.02408; found: 213.02487; *m*/*z* (%): 213 (2) [M^+], 178 (17) [M^+−Cl], 172 (100) [H$_2$C=N(*i*Pr)PCl$_2^+$].

Dichloro[isopropyl(prop-2-enyl)amino]phosphane (6d): Route B: 56% yield; b.p. 30 °C/1 mm Hg; ^{31}P NMR (C_6D_6): δ = 167.29 ppm; ^{13}C NMR (C_6D_6): δ = 136.30 (d, ^3J(C,P) = 3.7 Hz, CH=), 117.22 (s, =CH$_2$), 51.88 (d, ^2J(C,P) = 25.5 Hz, CHN), 47.92 (d, ^2J(C,P) = 11.5 Hz, CH_2N), 22.25 ppm (d, ^3J(C,P) = 9.6 Hz, CH$_3$); ^{1}H NMR (C_6D_6): δ = 5.61 (ddt, ^3J(H,H)-(*trans*) = 17.0 Hz, ^3J(H,H)(*cis*) = 10.2 Hz, ^3J(H,H) = 5.9 Hz, 1H; CH=), 4.87–4.97 (m, 2H; =CH$_2$), 3.46–3.58 (m, 3H; C*H*$_2$NC*H*), 0.89 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH$_3$); HRMS: *m*/*z* calcd for $C_6H_{12}NPCl_2$: 199.00845; found: 199.00513; MS: *m*/*z* (%): 199 (4) [M^+], 184 (100) [M^+ −CH$_3$], 108 (92) [$C_3H_6PCl^+$].

Dichloro[bis(but-3-enyl)amino]phosphane (13)

But-3-enylamine: $AlCl_3$ (8.00 g, 60 mmol) was added to a cooled (0 °C) suspension of $LiAlH_4$ (2.28 g, 60 mmol) in Et$_2$O (100 mL) and stirred at 0 °C for 10 min, after which a solution of allylcyanide (4.8 mL, 58 mmol) in Et$_2$O (60 mL) was added dropwise, followed by 1.5 h of stirring at 0 °C. The faint green mixture was made basic with 10% NaOH solution followed by continuous extraction of the water layer for four days. Drying and solvent evaporation gave a colorless liquid (2.65 g, 37.4 mmol, 64% yield). ^{1}H NMR ($CDCl_3$): δ = 5.76 (ddt, ^3J(H,H)(*trans*) = 17.1 Hz, ^3J(H,H)(*cis*) = 10.2 Hz, ^3J(H,H) = 6.9 Hz, 1H; CH=), 5.02–5.11 (m, 2H; CH$_2$=), 2.74 (t, ^3J(H,H) = 6.6 Hz, 2H; CH_2N), 2.18 (m, 2H; =CHC*H*$_2$), 1.1–1.2 ppm (br, 2H; NH$_2$).

Bis(but-3-enyl)amine: But-3-enylamine (2.28 g, 32 mmol), triethylamine (1.12 mL, 8 mmol), and 4-bromo-1-butene (0.80 mL, 8 mmol) were dissolved in Et$_2$O (6.5 mL) and refluxed for 3 h. At room temperature, HCl (15 mL, 4 N) was added and the water layer was extracted with diethyl ether (3×10 mL), neutralized, extracted again with diethyl ether, made basic (pH > 9), and once again extracted. The combined organic fractions were dried and evaporated. The crude product contained the desired product and some triethylamine. Since Et$_3$N was utilized as base in the subsequent reaction no further purification was attempted. Colorless liquid: 0.87 g (7.0 mmol, 88%); ^{13}C NMR ($CDCl_3$): δ = 136.51 (s, CH=), 116.24 (s, CH$_2$=), 48.77 (s, CH_2N), 34.33 ppm (s, *C*H$_2$CH=); ^{1}H NMR ($CDCl_3$):[27] δ = 5.75 (ddt, ^3J(H,H)(*trans*) = 17.1 Hz, ^3J(H,H)(*cis*) = 10.2 Hz, ^3J(H,H) = 6.8 Hz, 2H; CH=), 4.96–5.11 (m, 4H; CH$_2$=), 2.67 (t, ^3J(H,H) = 6.9 Hz, 4H; CH_2N), 2.18–2.28 (m, 4H; =CHC*H*$_2$), 0.8–1.1 ppm (br, 1H; NH).

*Dichloro[bis(but-3-enyl)amino]phosphane (**13**)*: Route B, 67% yield; b.p. 34–35 °C, 1–2 mm Hg; ^{31}P NMR (C_6D_6): δ = 163.31 ppm; ^{13}C NMR (C_6D_6): δ = 134.75 (s, CH=), 117.33 (s, CH$_2$=), 47.17 (d, ^2J(C,P) = 20.9 Hz, CH_2N), 32.71 ppm (d, ^3J(C,P) = 4.0 Hz, *C*H$_2$CH$_2$N); ^{1}H NMR (C_6D_6): δ = 5.47 (ddt, ^3J(H,H)(*trans*) = 17.0 Hz, ^3J(H,H)(*cis*) = 10.3 Hz, ^3J(H,H) = 6.8 Hz, 2H; CH=), 4.85–4.95 (m, 4H; CH$_2$=), 2.94 (dt, ^3J(H,P) = 13.0 Hz, ^3J(H,H) = 7.2 Hz, 4H; CH_2N), 1.90–1.98 ppm (m, 4H; C*H*$_2$CH$_2$N); HRMS: *m*/*z* calcd $C_8H_{14}NPCl_2$: 225.0241; found: 225.0237; MS: *m*/*z* (%): 225 (5) [M^+], 172 (100) [H$_2$C=N(*i*Pr)PCl$_2^+$], 130 (40) [CH$_2$NPCl$_2^+$].

Dichloro[isopropyl(6-phenylhex-5-ynyl)amino]phosphane (16a): Route B, 87%; b.p. 97–105 °C/5×10^{-3} mm Hg; ^{31}P NMR (C_6D_6): δ = 167.13 ppm (d, ^3J(P,H) = 10.1 Hz); ^{13}C NMR (C_6D_6): δ = 131.83 (s, *o*-ArC), 128.55 (s, *m*-ArC), 127.84 (s, *p*-ArC), 124.58 (s, *ipso*-ArC), 89.84 (s, CH$_2$*C*≡), 81.84 (s, ≡*C*Ph), 51.62 (d, ^2J(C,P) = 23.6 Hz, CHN), 45.02 (d, ^2J(C,P) = 13.5 Hz, CH_2N), 30.24 (d, ^3J(C,P) = 5.4 Hz, *C*H$_2$CH$_2$N), 26.22 (s, *C*H$_2$CH$_2$C≡), 22.27 (d, ^3J(C,P) = 9.0 Hz, CH$_3$), 19.24 ppm (s, *C*H$_2$C≡); ^{1}H NMR (C_6D_6): δ = 7.45 (m, 2H; *o*-ArH), 6.99–7.04 (m, 3H; *m*,*p*-ArH), 3.52 (d septet, ^3J(H,H) = ^3J(H,P) = 6.8 Hz, 1H; NCH), 2.89 (dt, ^3J(H,P) = 11.3 Hz, ^3J(H,H) = 7.6 Hz, 2H; NCH$_2$), 2.13 (t, ^3J(H,H) = 6.9 Hz, 2H; CH$_2$C≡), 1.46–1.58 (m, 2H; −C*H*$_2$CH$_2$N), 1.20–1.33 (m, 2H; C*H*$_2$CH$_2$C≡), 0.88 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH$_3$); HRMS: *m*/*z* calcd for $C_{15}H_{20}NPCl_2$: 315.07104; found: 315.07000; MS: *m*/*z* (%): 315 (6) [M^+],

280 (28) [M^+−Cl], 214 (32, [M^+−PCl_2], 198 (78) [$PhC_4H_4^+$], 156 (100) [M^+−*i*PrN(H)PCl_2].

Dichloro[isopropyl(5-phenylpent-4-ynyl)amino]phosphane (16b): Route B, 79%; b.p. 72–75°C/10^{-2} mm Hg; ^{31}P NMR ($CDCl_3$,): δ = 167.52 ppm (d, ^3J(P,H) = 10.1 Hz); ^{13}C NMR ($CDCl_3$): δ = 131.43 (s, *o*-ArC), 128.17 (s, *m*-ArC), 127.65 (s, *p*-ArC), 123.59 (s, *ipso*-ArC), 88.57 (s, $CH_2C\equiv$), 81.52 (s, $\equiv C$Ph), 51.77 (d, ^2J(C,P) = 24.9 Hz, CHN), 44.32 (d, ^2J(C,P) = 13.1 Hz, CH_2N), 29.81 (d, ^3J(C,P) = 5.3 Hz, CH_2CH_2N), 22.45 (d, ^3J(C,P) = 8.8 Hz, CH_3), 17.01 ppm (s, $CH_2C\equiv$); ^{1}H NMR (C_6D_6): δ = 7.46 (d, ^3J(H,H) = 7.2 Hz, 2H; *o*-ArH), 6.94–7.04 (m, 3H; *m*,*p*-ArH), 3.43–3.59 (m, 1H; CHN), 3.06 (dt, ^3J(H,P) = 11.1 Hz, ^3J(H,H) = 7.8 Hz, 2H; NCH_2), 2.08 (t, ^3J(H,H) = 6.9 Hz, 2H; $CH_2C\equiv$), 1.53–1.65 (m, 2H; CH_2CH_2N), 0.86 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; CH_3); HRMS: *m*/*z* calcd for $C_{14}H_{18}NPCl_2$: 301.05539; found: 301.05652; MS: *m*/*z* (%): 301 (<0.5) [M^+], 199 (84) [M^+−PhCCH], 127 (64) [M^+−$C_4H_{11}NPCl_2$], 114 (100) [$PhCCH^+$].

Dichloro[isopropyl(pent-3-ynyl)amino]phosphane (16c): Route A, 82%; b.p. 72°C/4 mm Hg; ^{31}P NMR (C_6D_6): δ = 164.97 ppm; ^{13}C NMR (C_6D_6): δ = 78.85 (d, ^4J(C,P) = 2.5 Hz, $=CCH_2$), 76.23 (s, Me*C*=), 51.51 (d, ^2J(C,P) = 18.2 Hz, CHN), 44.83 (d, ^2J(C,P) = 17.7 Hz, CH_2N), 21.12 (d, ^3J(C,P) = 7.3 Hz, $(CH_3)_2CH$), 22.02 (d, ^3J(C,P) = 4.8 Hz, $=CCH_2$), 3.34 ppm (s, $CH_3C=$); ^{1}H NMR (C_6D_6): δ = 3.56–3.71 (m, 1H; NCH), 3.01–3.12 (m, 2H; CH_2N), 2.11–2.20 (m, 2H; $=CCH_2$), 1.55 (t, ^5J(H,H) = 2.5 Hz, 3H; $=CCH_3$), 0.83 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; CH_3); HRMS: *m*/*z* calcd for $C_8H_{14}NPCl_2$: 225.0241; found: 225.02371; MS: *m*/*z* (%): 225 (6) [M^+], 190 (14) [M^+−Cl], 172 (100) [$H_2C=N(iPr)PCl_2^+$].

Dichloro[isopropyl(but-2-ynyl)amino]phosphane (16d): Route B, 53%; b.p. 50°C/5 mm Hg; ^{31}P NMR (C_6D_6): δ = 165.67 ppm; ^{13}C NMR (C_6D_6): δ = 80.67 (d, ^3J(C,P) = 1.1 Hz, $\equiv CCH_2$), 75.87 (d, ^4J(C,P) = 4.8 Hz, Me*C*≡), 52.03 (d, ^2J(C,P) = 24.6 Hz, CHN), 34.30 (d, ^2J(C,P) = 14.9 Hz, CH_2N), 21.92 (d, ^3J(C,P) = 9.3 Hz, $(CH_3)_2CH$), 3.19 ppm (s, $CH_3C\equiv$); ^{1}H NMR (C_6D_6): δ = 3.68–3.78 (m, 3H; CH_2NCH), 1.40 (t, ^5J(H,H) = 2.3 Hz, 3H; $CH_3C\equiv$), 0.97 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; $CH(CH_3)_2$); HRMS: *m*/*z* calcd for $C_7H_{12}NPCl_2$: 211.00845; found: 211.01042; MS: *m*/*z* (%): 211 (6) [M^+], 196 (100) [M^+−CH_3], 176 (56) [M^+−Cl].

General synthesis of bicyclic phosphiranes 7a–c and 14 and phosphirene 17a: A solution of the appropriate dichloroaminophosphane (1 mmol) in Et_2O (5 mL) was added to a cooled (−78°C) suspension of Collman's reagent (0.35 g, 1 mmol, $Na_2Fe(CO)_4$·1.5 dioxane) in Et_2O (10 mL). The resulting mixture was warmed to −30°C at which temperature reaction occurred, as indicated by the change in color to red, and stirred overnight. After filtration and solvent evaporation to dryness the oily residue was purified as indicated.

2-Isopropyl-2-aza-1-phosphabicyclo[5.1.0]octanetetracarbonyliron(0) (7a): Purification by flash chromatography (SiO_2, Et_2O/pentane = 3:100) at −15°C gave an orange oil. Yield: 53% (95% pure); ^{31}P NMR ($CDCl_3$, 298 K): δ = −41.34 ppm; ^{31}P NMR ($CDCl_3$, 220 K): δ = −34.5, −47.8 ppm; ^{13}C NMR (C_6D_6): δ = 214.03 (d, ^2J(C,P) = 23.9 Hz, CO), 53.42 (d, ^2J(C,P) = 3.3 Hz, $CH(CH_3)_2$), 46.91 (d, ^2J(C,P) = 3.4 Hz, CH_2N), 31.34 (d, ^3J(C,P) = 4.8 Hz, CH_2CH_2N), 28.89 (s, $CH_2CH_2CH_2$N), 27.06 (d, ^1J(C,P) = 8.2 Hz, PCH), 26.79 (d, ^2J(C,P) = 3.1 Hz, CH_2CHP), 25.12 (d, ^1J(C,P) = 13.4 Hz, PCH_2), 21.64 (d, ^3J(C,P) = 5.2 Hz, CH_3), 20.61 ppm (d, ^3J(C,P) = 2.1 Hz, CH_3); ^{1}H NMR ($CDCl_3$): δ = 3.13–3.32 (m, 1H; $CH(CH_3)_2$), 3.05–3.14 (m, 1H; HC*H*N), 2.71–2.81 (m, 1H; *H*CHN), 2.48–2.61 (m, 1H; HC*H*CH_2N), 2.07–2.16 (m, 1H; HC*H*−$(CH_2)_2$N), 1.70–1.77 (m, 2H; HC*H*CH(P), CH(P)), 1.34–1.64 (m, 4H; *H*CH-CH_2N, *H*CH-$(CH_2)_2$N, *H*CHCH(P), *endo*-PCH_2), 1.23 (d, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 1.12 (d, ^3J(H,H) = 6.5 Hz, 3H; CH_3), 1.19 ppm (br m, 1H; *exo*-PCH_2); IR (KBr): $\tilde{\nu}$ = 2048.5 (s), 1967.5 (sh), 1930.9 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{13}H_{18}FeNPO_4$: 339.03223; found: 339.02988; EI-MS *m*/*z* (%): 339 (8) [M^+], 227 (42) [M^+−4CO], 124 (28) [$C_8H_{12}N^+$], 70 (100) [$C_4H_8N^+$].

2-Isopropyl-2-aza-1-phosphabicyclo[4.1.0]heptanetetracarbonyliron(0) (7b): Crystallization (Et_2O, −80°C) gave yellow platelike crystals. Yield: 63%; m.p. 60–62°C (decomp); ^{31}P NMR (C_6D_6): δ = −45.17 ppm; ^{13}C NMR (C_6D_6): δ = 213.89 (d, ^2J(C,P) = 24.3 Hz, CO), 49.69 (d, ^2J(C,P) = 8.3 Hz, CHN), 40.29 (d, ^2J(C,P) = 4.6 Hz, CH_2N), 24.50 (d, ^3J(C,P) = 10.0 Hz, CH_2CH_2N), 23.55 (d, ^2J(C,P) = 4.3 Hz, CH_2CHP), 20.48 (d, ^3J(C,P) = 7.8 Hz, CH_3), 19.58 (s, CH_3), 18.99 (d, ^1J(C,P) = 22.9 Hz, PCH_2), 18.67 ppm (d, ^1J(C,P) = 1.6 Hz, PCH); ^{1}H NMR ($CDCl_3$): δ = 3.63–3.78 (m, 1H; CHN), 2.68–2.83 (m, 1H; HC*H*N), 2.51–2.64 (m, 1H; *H*CHN), 2.02–2.31 (m, 2H; CH_2CHP), 1.87–1.99 (m, 1H; CHP), 1.55–1.67 (m, 1H; HC*H*-CH_2N), 1.43–1.52 (m, 1H; *endo*-PCH_2), 1.12–1.39 (m, 1H; *H*CH-CH_2N), 1.09 (d, ^3J(H,H) = 6.6 Hz, 6H; $(CH_3)_2CH$), 0.82–0.91 ppm (m, 1H; *exo*-PCH_2); IR (KBr): $\tilde{\nu}$ = 2050 (m), 1969 (sh), 1937 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{12}H_{16}O_4NPFe$: 325.01657; found: 325.01796; *m*/*z* (%): 325 (9) [M^+], 213 (100) [M^+−4CO], 211 (20) [M^+−4CO−2H].

2-Isopropyl-2-aza-1-phosphabicyclo[3.1.0]hexanetetracarbonyliron(0) (7c): Distillation gave a yellow liquid. Yield: 64%; b.p. 33°C/5 × 10^{-3} mm Hg; ^{31}P NMR (C_6D_6): δ = −20.05 ppm; ^{13}C NMR (C_6D_6): δ = 213.06 (d, ^2J(C,P) = 24.4 Hz, CO), 45.34 (d, ^2J(C,P) = 6.2 Hz, CHN), 39.27 (s, CH_2N), 26.07 (s, CH_2CH_2N), 21.35 (d, ^3J(C,P) = 12.2 Hz, CH_3), 17.92 (s, CH_3), 15.85 (d, ^1J(C,P) = 8.0 Hz, PCH), 11.25 ppm (d, ^1J(C,P) = 26.6 Hz, PCH_2); ^{1}H NMR (C_6D_6): δ = 3.50–3.70 (m, 1H; CHN), 2.28–2.46 (m, 1H; *H*CHN), 1.71–1.83 (m, 1H; HC*H*N), 1.42–1.62 (m, 3H; CH_2CHP), 1.11–1.19 (m, 1H; *endo*-PCH_2), 0.85 (d, ^3J(H,H) = 6.7 Hz, 3H; CH_3), 0.77 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 0.18 ppm (ddd, ^2J(H,H) = ^3J(H,H) = 9.8 Hz, ^2J(H,P) = 2.7 Hz, 1H; *exo*-PCH_2); IR (KBr): $\tilde{\nu}$ = 2056 (s), 1981 (sh), 1942 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{11}H_{14}FeNO_4P$: 311.00157; found: 311.00092; MS: *m*/*z* (%): 311 (8) [M^+], 199 (100) [M^+−4CO], 157 (46) [M^+−4CO−C_3H_6], 128 (40) [M^+−4CO−C_4H_9N]; elemental analysis calcd (%) for $C_{11}H_{14}FeNO_4P$: C 42.47, H 4.54; found: C 42.50, H 4.65.

2-(But-3-enyl)-2-aza-1-phosphabicyclo[3.1.0]hexane tetracarbonyliron(0) (14): Distillation gave a yellow liquid. Yield: 71%; b.p. 30–33°C/5 × 10^{-3} mm Hg; ^{31}P NMR ($CDCl_3$): δ = −19.18 ppm; ^{13}C NMR ($CDCl_3$): δ = 212.63 (d, ^2J(C,P) = 23.9 Hz, CO), 135.40 (s, CH=), 116.74 (s, CH_2=), 47.38 (s, CH_2N(ring)), 46.37 (d, ^2J(C,P) = 5.2 Hz, CH_2N), 32.87 (d, ^3J(C,P) = 7.6 Hz, $CH_2C=$) 26.76 (d, ^2J(C,P) = 3.0 Hz, CH_2CH_2N(ring)), 17.10 (d, ^1J(C,P) = 6.9 Hz, PCH), 11.47 ppm (d, ^1J(C,P) = 26.0 Hz, PCH_2); ^{1}H NMR ($CDCl_3$): δ = 5.79 (ddt, ^3J(H,H)(*trans*) = 17.1 Hz, ^3J(H,H)(*cis*) = 10.2 Hz, ^3J(H,H) = 6.9 Hz, CH=), 5.09 (dd, ^2J(H,H) = 1.4 Hz, ^3J(H,H) = 17.1 Hz, $=CH_{trans}$), 5.04 (m, $=CH_{cis}$), 3.06–3.22 (m, 2H; $CHNCH$), 2.81–2.89 (m, 1H; −C*H*N), 2.50–2.57 (m, 1H; ring-C*H*N-*endo*), 2.81–2.43 (m, 4H; CH_2CH_2N), 2.11 (m, 1H; CHP), 1.75 (m, 1H; PCH_2-*endo*), 0.61 ppm (ddd, ^3J(H,H) = 9.8 Hz, ^2J(H,P) = 9.8 Hz, ^2J(H,H) = 2.7 Hz, PCH_2-*exo*); IR (KBr): $\tilde{\nu}$ = 2056.25 (s), 1952.08 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd $C_{11}H_{14}FeNO_3P$: 295.0061; found: 295.0071 [M^+−CO]; MS: *m*/*z* (%): 295 (19) [M^+−CO], 211 (100) [M^+−4CO].

8-Phenyl-2-isopropyl-2-aza-1-phosphabicyclo[5.1.0]oct-7-ene tetracarbonyliron(0) (17a): Purification by flash column chromatography at −15°C (SiO_2, 6.7% Et_2O in pentane, R_f = 0.46). Yellow oil (60% yield); crystallization (Et_2O, −80°C): bright yellow plate-like crystals; m.p. 70–71°C (decomp); ^{31}P NMR (C_6D_6): δ = −42.56 ppm; ^{13}C NMR (C_6D_6): δ = 214.27 (d, ^2J(C,P) = 24.6 Hz, CO), 147.84 (d, ^1J(C,P) = 37.0 Hz, =*C*Ph), 143.32 (d, ^1J(C,P) = 5.5 Hz, $CH_2C=$), 130.19 (s, *p*-ArC), 129.85 (d, ^2J(C,P) = 2.4 Hz, *ipso*-ArC), 129.51 (d, ^3J(C,P) = 3.9 Hz, *o*-ArC), 129.37 (s, *m*-ArC), 47.13 (d, ^2J(C,P) = 10.2 Hz, CHN), 43.54 (d, ^2J(C,P) = 5.1 Hz, CH_2N), 31.87 (CH_2CH_2N), 27.46 (d, ^2J(C,P) = 2.6 Hz, $CH_2C=$), 26.57 (s, $CH_2CH_2C=$), 21.02 (d, ^3J(C,P) = 9.9 Hz, CH_3), 20.48 ppm (s, CH_3); ^{1}H NMR (C_6D_6): δ = 7.48 (d, ^3J(H,H) = 7.1 Hz, 2H; *o*-ArH), 7.09 (m, 2H; *m*-ArH), 7.01 (m, 1H; *p*-ArH), 4.14–4.24 (m, 1H; NCH), 2.90 (dddd, ^3J(H,P) = 29.1 Hz, ^2J(H,H) = 13.0 Hz, ^3J(H,H) = 5.4 Hz, ^3J(H,H) = 2.0 Hz, 1H; HCC=), 2.40–2.54 (m, 2H; H(CH)N, HCC=), 1.46–1.62 (m, 3H; H(CH)N, *H*(CH)CH_2N, *H*(CH)CH_2CH_2N), 0.75–1.03 (m, 2H; *H*(CH)CH_2N, *H*(CH)CH_2CH_2N), 0.93 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 0.80 ppm (d, ^3J(H,H) = 6.7 Hz, CH_3); IR (KBr): $\tilde{\nu}$ = 2048.5 (s), 1967.5 (sh), 1940.5 cm^{-1} (s) (C=O); HRMS: calcd for $C_{19}H_{20}FeNPO_4$: 413.04791; found: 413.04596; MS: *m*/*z* (%): 413 (<1) [M^+], 301 (20) [M^+−4CO], 105 (65) [$C_4H_{10}NP^+$], 72 (69) [$C_4H_{10}N^+$], 55 (66) [$C_3H_5N^+$], 41 (100) [$C_3H_5^+$].

7-Phenyl-2-isopropyl-2-aza-1-phosphabicyclo[4.1.0]hept-6-enetetracarbonyliron(0) (17b): A cooled (−10°C) solution of **16b** (0.61 g, 2.0 mmol) in Et_2O (65 mL) was added dropwise over 2.5 h to a cooled (−10°C) suspension of Collman's reagent (0.78 g, 2.3 mmol) in Et_2O (20 mL). The solution was warmed to 0°C, stirred for 45 min and then concentrated, filtered, and evaporated to dryness at 0°C. Purification was performed by

column chromatography at −15 °C (SiO_2, 6% Et_2O in pentane, R_f = 0.30). Unstable red-brown oil, (0.22 g, 0.56 mmol, 28%, 95% pure); ^{31}P NMR (C_6D_6): δ = −41.15 ppm; ^{13}C NMR (C_6D_6): δ = 214.13 (d, $^2J(C,P)$ = 24.5 Hz, CO), 154.64 (d, $^1J(C,P)$ = 48.6 Hz, =*C*Ph), 146.62 (d, $^1J(C,P)$ = 6.0 Hz, CH_2C=), 130.20 (s, *p*-ArC), 129.37 (s, *m*-ArC), 129.15 (d, $^3J(C,P)$ = 3.1 Hz, *o*-ArC), 46.32 (d, $^2J(C,P)$ = 5.5 Hz, CHN), 40.21 (d, $^2J(C,P)$ = 5.1 Hz, CH_2N), 31.72 (d, $^2J(C,P)$ = 8.6 Hz, CH_2C=), 28.00 (s, CH_2CH_2N), 20.22 (d, $^3J(C,P)$ = 10.3 Hz, CH_3), 20.04 ppm (s, CH_3); ^1H NMR (C_6D_6), not all assignments could be made due to instability of the product: δ = 7.47 (d, $^3J(H,H)$ = 7.1 Hz, 2H; *o*-ArH), 7.01–7.15 (m, 3H; *m*+*p*-ArH), 3.77–3.87 (m, 1H; CHN), 2.75–2.83 (m, 1H), 2.3–2.7 (m, 1H), 1.98–2.07 (m, 1H), 1.77–1.83 (m, 2H), 1.21–1.29 (m, 1H), 0.81 (d, $^3J(H,H)$ = 6.5 Hz, 3H; CH_3), 0.71 ppm (d, $^3J(H,H)$ = 6.6 Hz, 3H; CH_3).

Phosphinidene exchange reactions in phenylacetylene

1-[Isopropyl(pent-4-enyl)amino]-2-phenylphosphirenetetracarbonyliron(0) (8b): The reaction of **8b** (0.23 g, 0.70 mmol) with phenylacetylene (1.9 mL, 17 mmol) at room temperature in the dark, monitored by ^{31}P NMR spectroscopy, and after removal of the solvent in vacuo, gave the crude product (0.37 g) after 4 h. Chromatography (SiO_2, 3% Et_2O in pentane) at −15 °C gave **8b** as an orange oil (0.17 g, 0.40 mmol, 57% yield). ^{31}P NMR (C_6D_6): δ = −36.34 ppm; ^{13}C NMR (C_6D_6): δ = 214.05 (d, $^2J(C,P)$ = 24.2 Hz, CO), 159.03 (d, $^1J(C,P)$ = 19.3 Hz, Ph*C*=), 139.85 (s, CH_2=*C*H), 135.08 (d, $^1J(C,P)$ = 2.0 Hz, =C(P)H), 131.31 (s, *p*-ArC), 129.36 (s, *m*-ArC), 129.31 (d, $^3J(C,P)$ = 3.8 Hz, *o*-ArC), 127.92 (s, *ipso*-ArC), 115.15 (s, CH_2=), 48.20 (d, $^2J(C,P)$ = 10.5 Hz, CHN), 40.82 (d, $^2J(C,P)$ = 1.4 Hz, CH_2N), 32.30 (d, $^3J(C,P)$ = 1.4 Hz, CH_2CH_2N), 31.34 (s, *C*H$_2$C=), 21.67 (d, $^3J(C,P)$ = 6.6 Hz, CH_3), 21.28 ppm (d, $^3J(C,P)$ = 3.8 Hz, CH_3); ^1H NMR (C_6D_6): δ = 8.05 (d, $^2J(H,P)$ = 16.0 Hz, 1H; =C(P)H), 7.54–7.49 (m, 2H; *o*-ArH), 6.99–7.05 (m, 3H; *m*+*p*-ArH), 5.45–5.61 (m, 1H; CH_2=C*H*), 4.82–4.91 (m, 2H; CH_2=), 4.11 (dseptet, $^2J(H,P)$ = $^3J(H,H)$ = 6.7 Hz, 1H; CHN), 2.34 (m, 2H; CH_2N), 1.64–1.74 (m, 2H; CH_2CH=), 1.26–1.35 (m, CH_2CH$_2$N), 0.89 (d, $^3J(H,H)$ = 6.7 Hz, CH_3), 0.88 ppm (d, $^3J(H,H)$ = 6.7 Hz, CH_3); IR (KBr): $\tilde{\nu}$ = 2050.5 (s), 1973.3 (sh), 1940.5 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{18}H_{22}FeNO_2P$: 371.0737; found: 371.07066 [M^+−2CO]; MS: *m*/*z* (%): 371 (4) [M^+−2CO], 315 (100) [M^+−4CO], 102 (45) [PhCCH$^+$].

1-[Isopropyl(but-3-enyl)amino]-2-phenylphosphirenetetracarbonyliron(0) (8c): A similar procedure was followed as described for **8b**. The reaction was completed after 6 days to give **8c** as an orange oil (76%). ^{31}P NMR (C_6D_6): δ = −36.51 ppm; ^{13}C NMR ($CDCl_3$): δ = 213.51 (d, $^2J(C,P)$ = 24.2 Hz, CO), 159.00 (d, $^1J(C,P)$ = 20.7 Hz, Ph*C*=), 135.01 (s, CH_2=*C*H), 134.31 (s, =C(P)H), 131.29 (s, *p*-ArC), 129.24 (d, $^3J(C,P)$ = 4.3 Hz, *o*-ArC), 129.23 (s, *m*-ArC), 127.66 (s, *ipso*-ArC), 116.59 (s, CH_2=), 47.98 (d, $^2J(C,P)$ = 10.5 Hz, CHN), 40.65 (s, CH_2N), 37.39 (s, =CCH_2), 21.82 (d, $^3J(C,P)$ = 6.7 Hz, CH_3), 21.38 ppm (d, $^3J(C,P)$ = 3.1 Hz, CH_3); ^1H NMR (C_6D_6): δ = 8.04 (d, $^2J(H,P)$ = 16.1 Hz, 1H; =C(P)H), 7.44–7.49 (m, 2H; *o*-ArH), 6.99–7.08 (m, 3H; *m*+*p*-ArH), 5.47 (ddt, $^3J(H,H)$(*trans*) = 17.0 Hz, $^3J(H,H)$(*cis*) = 10.3 Hz, $^3J(H,H)$ = 6.8 Hz, 1H; CH_2=C*H*), 4.80–4.91 (m, 2H; CH_2=), 4.05–4.15 (m, 1H; CHN), 2.34–2.47 (m, 2H; CH_2N), 1.89–1.98 (m, 2H; CH_2CH=), 0.87 (d, $^3J(H,H)$ = 6.7 Hz, 3H; CH_3), 0.86 ppm (d, $^3J(H,H)$ = 6.7 Hz, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 2052.4 (s), 2015.7 (sh), 1965.6 (sh), 1944.4 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{18}H_{20}FeNO_3P$: 385.0530; found: 385.05109 [M^+−CO]; MS: *m*/*z* (%): 385 (5) [M^+−CO], 301 (64) [M^+−4CO], 199 (100) [M^+−4CO−PhCCH], 102 (73) [PhCCH$^+$].

1-[Isopropyl(prop-2-enyl)amino]-2-phenylphosphirenetetracarbonyliron(0) (8d): A solution of dichloroaminophosphane **6d** (1 mmol) and phenylacetylene (0.95 mmol) in Et_2O (2.5 mL) was added to a cooled (−78 °C) suspension of Collman's reagent (0.33 g, 0.95 mmol) in Et_2O (20 mL). The resulting mixture was warmed to −30 °C at which temperature reaction occurred, as indicated by the color change to red. Filtration at 0 °C, concentration to 1 mL, and flash chromatography over silica (3% Et_2O in pentane) at −5 °C gave **8d** as a red oil (213 mg, 0.53 mmol, 56%). ^{31}P NMR ($CDCl_3$): δ = −34.74 ppm; ^{13}C NMR ($CDCl_3$): δ = 213.44 (d, $^2J(C,P)$ = 24.2 Hz, CO), 158.68 (d, $^1J(C,P)$ = 19.7 Hz, Ph*C*=), 137.87 (s, CH_2=*C*H), 134.91 (s, PhC=*C*H), 131.21 (s, *p*-ArC), 129.24 (d, $^3J(C,P)$ = 4.6 Hz, *o*-ArC), 129.18 (s, *m*-ArC), 127.87 (s, *ipso*-ArC), 115.57 (s, CH_2=), 48.10 (d, $^2J(C,P)$ = 10.4 Hz, CHN), 43.37 (s, CH_2N), 21.65 (d, $^3J(C,P)$ = 6.7 Hz, CH_3), 21.30 ppm (d, $^3J(C,P)$ = 2.7 Hz, CH_3); ^1H NMR ($CDCl_3$): δ = 8.66 (d, $^2J(H,P)$ = 15.5 Hz, 1H; =C(P)H), 7.47–7.65 (m, 5H; ArH), 5.59–5.74 (m, 1H; CH_2=C*H*), 5.03–5.17 (m, 2H; CH_2=), 4.09–4.26 (m, 1H; CHN), 3.18–3.43 (m, 2H; CH_2N), 1.10 ppm (d, $^3J(H,H)$ = 6.0 Hz, 6H; CH_3); IR (KBr): $\tilde{\nu}$ = 2050.5 (s), 1971.4 (sh), 1942.4 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{17}H_{18}FeNO_3P$: 371.0374; found: 371.03446 [M^+−CO]; MS: *m*/*z* (%): 371 (15) [M^+−CO], 287 (70) [M^+−4CO], 183 (100) [M^+−4CO−C_8H_8], 102 (50) [PhCCH$^+$].

1-[Isopropyl(5′-phenylpent-4′-ynyl)amino]-2-phenylphosphirenetetracarbonyliron(0) (18b): A cooled (−10 °C) solution of **16b** (0.30 g, 1.0 mmol) in Et_2O (35 mL) was added dropwise over 2.5 h to a cooled (−10 °C) suspension of Collman's reagent (0.31 g, 1.0 mmol) in Et_2O (35 mL). The solution was warmed to 0 °C, stirred for 45 min and then concentrated, filtered, and evaporated to a minimal volume at 0 °C. Phenylacetylene (4 mL) was added and, after 10 min stirring at room-temperature, was removed under high vacuum at 35 °C. Purification by flash column chromatography (SiO_2, 5% Et_2O in pentane) yielded **18b** as a red-brown oil (53 mg, 0.11 mmol, 12%). ^{31}P NMR ($CDCl_3$): δ = −36.28 ppm; ^{13}C NMR ($CDCl_3$): δ = 213.44 (d, $^2J(C,P)$ = 24.1 Hz, CO), 159.08 (d, $^1J(C,P)$ = 23.2 Hz, =*C*-Ph), 133.82 (s, HC=), 131.44 (s, *o*-Ar-C≡), 131.22 (s, *p*-Ar-C=), 129.19 (d, $^3J(C,P)$ = 4.6 Hz, *o*-Ar-C=), 129.16 (s, *m*-Ar-C=), 128.23 (s, *m*-Ar-C≡), 127.68 (s, *p*-Ar-C≡), 127.60 (d, $^2J(C,P)$ = 2.9 Hz, *ipso*-Ar-C=), 123.65 (s, *ipso*-Ar-C≡), 89.02 (s, CH_2C≡), 81.29 (s, ≡*C*Ph), 47.94 (d, $^2J(C,P)$ = 10.7 Hz, CHN), 40.09 (s, CH_2N), 31.54 (s, *C*H$_2$CH$_2$N), 21.83 (d, $^3J(C,P)$ = 7.7 Hz, CH_3), 21.17 (d, $^3J(C,P)$ = 2.6 Hz, CH_3), 16.76 ppm (s, *C*H$_2$C≡); ^1H NMR ($CDCl_3$): δ = 8.78 (d, $^2J(H,P)$ = 16.3 Hz, 1H; =C(P)H), 7.61–7.65 (m, 2H; =C-(*o*-ArH)), 7.46–7.48 (m, 3H; =C-(*m*,*p*-ArH)), 7.35–7.38 (m, 2H; ≡C-(*o*-ArH)), 7.28–7.31 (m, 3H; ≡C-(*m*,*p*-ArH)), 4.15–4.26 (m, 1H; CHN), 2.73–2.86 (m, 1H; 2H; CH_2N), 2.24–2.42 (m, 2H; CH_2C≡), 1.61–1.73 (m, 2H; CH_2CH$_2$N), 1.18 (d, $^3J(H,H)$ = 6.8 Hz, 3H; CH_3), 1.14 ppm (d, $^3J(H,H)$ = 6.9 Hz, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 2050.5 (s), 1973.3 (sh), 1930.9 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{23}H_{24}FeNPO$: 417.0945; found: 417.0907 [M^+−3CO]; MS: *m*/*z* (%): 417 (12) [M^+−3CO], 387 (20) [M^+−4CO], 159 (42) [M^+−4CO−$C_{18}H_{12}$], 102 (100) [PhCCH$^+$].

1-[Isopropyl(but-2-ynyl)amino]-2-phenylphosphirenetetracarbonyliron(0) (18d): A solution of **16d** (0.41 g, 1.2 mmol) was added to a cooled (−78 °C) suspension of Collman's reagent (0.41 g, 1.2 mmol) and phenylacetylene (0.13 mL, 1.2 mmol) in Et_2O (25 mL). The reaction mixture was warmed to −30 °C and then warmed to room temperature overnight. Filtration, solvent evaporation, and flash column chromatography at 5 °C (SiO_2, 5% Et_2O in pentane) yielded **18d** as a red-brown oil (110 mg, 0.27 mmol, 23%). ^{31}P NMR ($CDCl_3$): δ = −34.48 ppm; ^{13}C NMR ($CDCl_3$,): δ = 213.34 (d, $^2J(C,P)$ = 24.1 Hz, CO), 161.11 (d, $^1J(C,P)$ = 18.3 Hz, =*C*Ph), 134.24 (s, =CH), 131.08 (s, *p*-Ar), 129.35 (d, $^3J(C,P)$ = 4.8 Hz, *o*-Ar), 129.00 (s, *m*-Ar), 128.14 (s, *ipso*-Ar), 79.37 (s, ≡*C*CH$_2$), 78.18 (s, $^4J(C,P)$ = 2.3 Hz, Me*C*≡), 48.51 (d, $^2J(C,P)$ = 8.1 Hz, CHN), 31.53 (s, CH_2N), 21.42 (d, $^3J(C,P)$ = 3.5 Hz, CH_3), 21.32 (s, CH_3), 3.15 ppm (s, *C*H$_3$C≡); ^1H NMR ($CDCl_3$): δ = 8.75 (d, $^2J(H,P)$ = 15.7 Hz, 1H; =C(P)H), 7.48–7.72 (m, 5H; ArH), 4.02 (m, 1H; CHN), 3.52 (m, 2H; CH_2N), 1.52 (s, 3H; ≡CCH_3), 1.17 (d, $^3J(H,H)$ = 6.6 Hz, 3H; CH_3), 1.11 ppm (d, $^3J(H,H)$ = 6.6 Hz, 3H; CH_3); IR (KBr): $\tilde{\nu}$ = 2052.4 (s), 1979.1 (s), 1930.9 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{18}H_{18}FeNO_3P$: 383.03737; found: 383.03945 [M^+−CO]; MS: *m*/*z* (%): 383 (3) [M^+−CO], 299 (100) [M^+−4CO], 197 (52) [M^+−4CO−PhC=CH].

2,8-Diisopropyl-6,12-dimethyl-2,8-aza-1,7-diphosphatricyclo[9.1.0.0^{5,7}]-dodeca-5,11-dienebis[tetracarbonyliron(0)] (19): A cooled (−30 °C) solution of **16c** (0.45 g, 2.0 mmol) in Et_2O (50 mL) was added dropwise over 35 min to a cooled (−20 °C) suspension of Collman's reagent (0.70 g, 2.0 mmol) in Et_2O (25 mL). Filtration, solvent evaporation, and column chromatography (SiO_2, Et_2O/pentane = 3:100) yielded a yellow solid (8%). Crystallization (Et_2O, −78 °C) gave small, plate-like yellow crystals. M.p. 124 °C (decomp); ^{31}P NMR (C_6D_6): δ = −35.30 ppm; ^{13}C NMR (C_6D_6): δ = 214.09 (d, $^2J(C,P)$ = 24.0 Hz, CO), 153.34 (d, $^1J(C,P)$ = 19.4 Hz, =*C*Me), 150.44 (s, *C*=CMe), 48.95 (d, $^2J(C,P)$ = 9.4 Hz, CHN), 39.42 (s, CH_2N), 28.68 (t, $^2J(C,P)$ = $^3J(C,P)$ = 3.7 Hz, CH_2C=), 22.28 (d, $^3J(C,P)$ = 9.0 Hz, *C*H$_3$CH), 20.28 (d, $^3J(C,P)$ = 1.8 Hz, *C*H$_3$CH),

11.39 ppm (d, ^2J(C,P) = 2.8 Hz, =CCH$_3$); ^{1}H NMR (C_6D_6): δ = 3.86–4.02 (m, 2H; CHN), 2.45–2.72 (m, 4H; CH_2N), 2.23–2.41 (m, 4H; CH_2C=), 1.87 (d, ^3J(H,P) = 10.5 Hz, 6H; =CCH$_3$), 0.96 (d, ^3J(H,H) = 6.8 Hz, 6H; CH_3), 0.94 ppm (d, ^3J(H,H) = 6.6 Hz, 6H; CH_3); IR (KBr): $\tilde{\nu}$ = 2045 (s), 1954 (s), 1929 cm^{-1} (s) (C=O); HRMS: *m*/*z* calcd for $C_{22}H_{28}Fe_2N_2O_6P_2$: 590.0121; found 590.0096 [M^+ −2CO]; *m*/z (%): 590 (4) [M^+ −2CO], 506 (46) [M^+ −5CO], 478 (10) [M^+ −6CO], 422 (100) [M^+ −8CO].

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[12] Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The structures were determined with automated Patterson methods[28] and refined with SHELXL97[29] against F^2 for all reflections. Illustrations, structure calculations, and checking were performed with the PLATON package.[30] Compound **7b**: $C_{12}H_{16}FeNO_4P$, M_r = 325.08, yellow plates, 0.30 × 0.24 × 0.12 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 8.2860(1), b = 14.8128(2), c = 11.8843(1) Å, β = 94.1417(5)°, V = 1454.86(3) Å^3, Z = 4, ρ_{calcd} = 1.484 g cm^{-3}; 23129 reflections were measured, of which 3326 were unique. Absorption correction was based on multiple measured reflections (μ = 1.15 mm^{-1}, correction range 0.59–0.87). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined freely with isotropic displacement parameters. 236 refined parameters, no restraints. R indices [$I > 2\sigma(I)$]: R_1 = 0.0277, wR_2 = 0.0609. R indices (all data): R_1 = 0.0456, wR_2 = 0.0683; S = 1.077. Residual electron density between −0.28 and 0.37 e Å^{-3}. Compound **17a**: $C_{19}H_{20}FeNO_4P$, M_r = 413.18, yellow blocks, 0.30 × 0.15 × 0.15 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 8.6320(2), b = 10.8710(3), c = 11.4937(3) Å, α = 98.1520(14), β = 111.7000(18), γ = 91.9060(9)°, V = 987.68(5) Å^3, Z = 2, ρ_{calcd} = 1.389 g cm^{-3}, μ = 0.87 mm^{-1}. 14258 reflections were measured, of which 4459 were unique. An absorption correction was not considered necessary. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent parameter of their carrier atoms. 237 refined parameters, no restraints. R indices [$I > 2\sigma(I)$]: R_1 = 0.0340, wR_2 = 0.0841. R-indices (all data): R_1 = 0.0470, wR_2 = 0.0897; S = 1.031. Residual electron density between −0.48 and 0.45 e Å^{-3}. Compound **19**: $C_{24}H_{28}Fe_2N_2O_8P_2$, M_r 646.12, colorless plates, 0.36 × 0.27 × 0.12 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 9.6901(7), b = 15.5833(15), c = 10.2081(9) Å, β = 113.803(6)°, V = 1410.3(2) Å^3, Z = 2, ρ_{calcd} = 1.521 g cm^{-3}. 15476 reflections were measured, of which 3229 were unique. Absorption correction based on multiple measured reflections (μ = 1.19 mm^{-1}, correction range 0.65–0.87). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent parameter of their carrier atoms. 175 refined parameters, no restraints. R indices [$I > 2\sigma(I)$]: R_1 = 0.0267, wR_2 = 0.0618. R-indices (all data): R_1 = 0.0360, wR_2 = 0.0648. S = 1.090. Residual electron density between −0.27 and 0.34 e Å^{-3}. CCDC-256107 (**7b**), 256108 (**17a**), and 256109 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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