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Methylene-Azaphosphirane as a Reactive Intermediate

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Abstract: Reaction of the transient phosphinidene complexes R-P=$W(CO)_5$ with N-substituted-diphenylketenimines leads unexpectedly to the novel 2-aminophosphindoles, as confirmed by an X-ray crystal structure determined for one of the derivatives. Experimental evidence for a methylene-azaphosphirane intermediate was found by using the iron-complexed phosphinidene iPr_2N-P=$Fe(CO)_4$, which affords the 2-aminophosphindole together with the novel methylene-2,3-dihydro-1*H*-benzo[1,3]azaphosphole. Analysis of the reaction pathways with DFT indicates that the initially formed methylene-azaphosphirane yields both phosphorus heterocycles by way of a [1,5]- or [1,3]-sigmatropic shift, respectively, followed by a H-shift. Strain underlies both rearrangements, which causes these remarkably selective conversions that can be tuned by changing the substituents.

Keywords: density functional calculations · methylene cyclopropane · heterocycles · reaction mechanisms · reactive intermediates

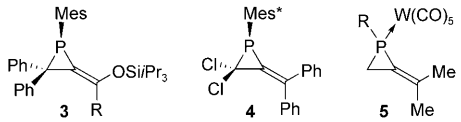
Introduction

Ring strain augmented by the presence of an exocyclic double bond makes the heteroatom analogues of methylenecyclopropane fascinating compounds.[1] Strain underlies, for example, the biradical interconversion of the valence isomers **1** and **2**, which are well-established reactive intermediates.[2] As expected, bulky substituents on the heteroatom, ring and/or double bond stabilize the aziridines, oxiranes and thiiranes derivatives, which are accessible via thermally or photochemically induced ring closures, rather then by, for example, epoxidation of or nitrene addition to allenes.[1,3]

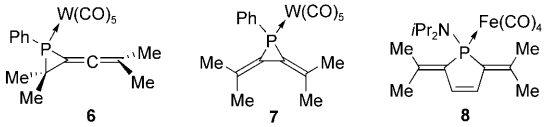
X = O, N, S, SO, SO_2

Phosphorus derivatives are similarly accessible, such as the thermal N_2 extrusion of a diazaphosphole that gives **3**,[4] but also by addition of dichlorocarbene to a 1-phosphaallene that gives **4**.[5] Recently, we and others have shown that very stable non-congested methylenephosphiranes, such as **5**, can be obtained by the carbene-like addition of electrophilic phosphinidene complexes R-P=$W(CO)_5$[6] to allenes.[7] From cumulenes even stable vinylidenephosphiranes **6** and phospha[3]radialenes **7** were synthesized by this route.[8] Diallenes also give 1,2-adducts, but these convert to dimethylenephospholes **8**[9] via a [1,3]-sigmatropic shift.[10]

Alkylidenecyclopropanes with a second heteroatom in the ring are scarcer and the few that are known as intermediates



Mes* = 2,4,6-tri-*tert*-butylphenyl



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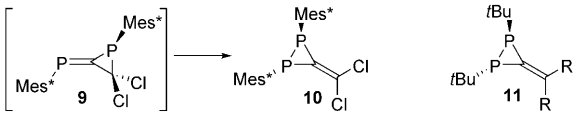
are highly congested.[10] Of those containing two phosphorus atoms, methylenediphosphirane **10** is stable and was obtained by Yoshifuji et al. by dichlorocarbene addition to a 1,3-diphosphaallene followed by rearrangement of **9**,[5,12] while Baudler used a condensation route for the synthesis of **11**.[13] Related systems with the second heteroatom not being phosphorus are very limited.[14] Could they be accessible by 1,2-addition of a phosphinidene to heteroallenes? This is the topic of the present study in which we focus on ketenimines.



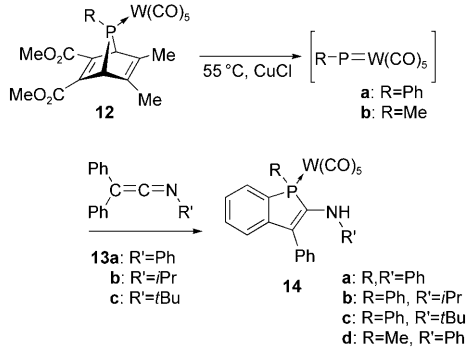
Ketenimines are readily accessible, useful building blocks in organic synthesis that have been widely applied for the synthesis of heterocycles[15] because of their ability to participate in [2+2]-cycloadditions through either the C=N or C=C bond.[16] Their reactivity toward carbenes[17] and electrophilic reagents has, however, hardly been addressed.[18]

Results and Discussion

The discussion is structured as follows. First, the experimental results are presented for the reaction of phosphinidene complexes with various ketenimines. In this section it is made plausible that alkylidene-azaphosphiranes[19] are intermediates for the formation of the observed 2-aminophosphindole products. In the next section, this premise will be supported by a survey of the potential energy surface using density functional theory.

Synthesis: Reaction of the terminal phosphinidene complexes R-P=W(CO)$_5$ (R = Ph, Me), generated in situ at 55 °C by the CuCl-catalyzed decomposition[20] of its 7-phosphanorbornadiene precursor **12**,[21] with N-substituted-diphenylketenimines **13** resulted in the fully unexpected formation of the novel 2-aminophosphindoles **14** as sole products in moderate to excellent yields (39–91 %, Scheme 1). No intermediates could be detected by ^{31}P NMR spectroscopy. Given that in all cases one of the phenyl groups becomes P-substituted, these mild reactions are remarkably selective.

This selectivity extends to bisketenimines as reaction of **15** with two equivalents of Ph-P=W(CO)$_5$, at 110 °C, without the use of the CuCl catalyst, results in the formation of bisphosphindoles **16** in 49 % yield as a 1:1 mixture of diastereomers (Scheme 2). The structure of C_2-symmetrical complex **16a** was established unequivocally by a single-crystal X-ray structure determination (Figure 1),[22] showing the central phenyl ring with each of the *para*-amino substituents carrying a W(CO)$_5$-complexed phosphindole. The P–C bonds of **16a** are of normal lengths (P1–C1 1.842(3), P1–C8 1.826(4) and P1–C9 1.838(3) Å), whereas the C–N bonds



Scheme 1. Synthesis of 2-aminophosphindoles **14**.

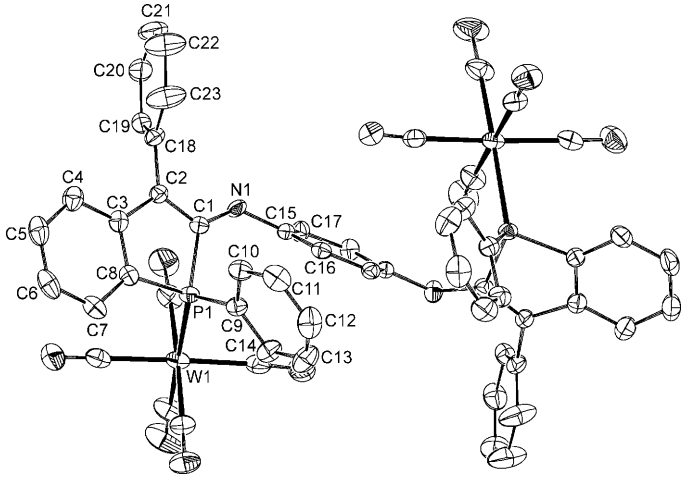
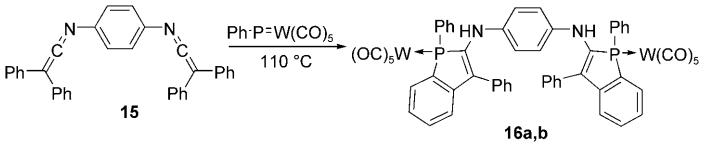


Figure 1. Displacement ellipsoid plot of **16a** with ellipsoids set at the 50 % probability level. The molecule is located on an exact, crystallographic C_2 axis. Hydrogen atoms are omitted for clarity and only one orientation of the disordered phenyl group at C2 is displayed. Selected bond lengths [Å], angles and torsion angles [°]: W1–P1 2.5156(8), P1–C1 1.842(3), P1–C8 1.826(4), P1–C9 1.838(3), N1–C1 1.373(4), N1–C15 1.410(4), C1–C2 1.354(4), C2–C3 1.468(4), C3–C8 1.401(4); C1-P1-C8 89.92(14), C1-N1-C15 129.6(3); C1-C2-C3-C8 –1.0(4).



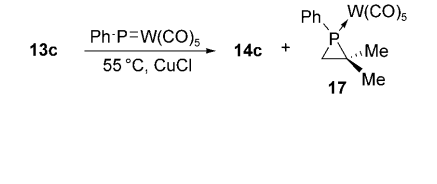
Scheme 2. Synthesis of bis-phosphindoles **16**.

are rather short (N1–C1 1.373(4), N1–C15 1.410(4) Å), but similar to those observed in *N,N′*-diphenyl-1,4-phenylenediamine.[23] The planar phosphole ring with its normal C1-P1-C8 bond angle of 89.92(14)° shows no signs of ring strain.

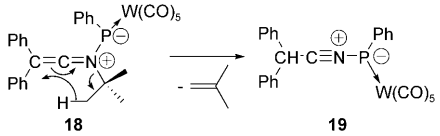
The ^{31}P NMR chemical shift of the 2-aminophosphindoles is sensitive to the P-substituent (Ph or Me); **14a–c** and **16** with a phenyl group are more deshielded (δ 12.9–17.4, ^1J(P,W) = 230–234 Hz) than **14d** with its methyl group (δ 3.0 ppm, ^1J(P,W) = 226.3 Hz).[24] The presence of the R′-NH group is evident from the sharp ^{1}H NMR resonance at δ

5.6–5.8 with a typical ^3J(H,P) coupling constant of 11–13 Hz for R′ = phenyl or at δ 3.7–3.8 (^3J(H,P) = 20–23 Hz) for R′ = alkyl (*i*Pr, *t*Bu).

Only in one case, using *N*-*tert*-butyl-diphenylketenimine (**13c**), the formation of the phosphindole (**14c**, 39%) was accompanied with a byproduct (13%) that was identified as phosphirane **17** based on its ^{31}P NMR resonance at δ −142.8 (Scheme 3).[25] It must originate from reaction of the phosphinidene complex with isobutene that is formed during the reaction. However, ketenimine **13c** is stable under the reaction conditions (55°C, CuCl) in the absence of precursor **12a**; only at elevated temperatures (125°C) **13c** does decompose into isobutene and diphenylacetonitrile.[26] A more likely source is an intermediate iminium ion as quaternary *tert*-butyl-ammonium ions release isobutene even at room temperature.[27] Such a species, P,N-ylide **18**, would form on adding the phosphinidene complex to the nitrogen atom of the ketenimine. P,N-Ylides have been postulated in reactions of phosphinidenes with imines.[28] A subsequent ene-type H-shift would release isobutene and form ylide **19** that can regenerate Ph-P=W(CO)$_5$ by liberating diphenylacetonitrile[29] that was indeed detected in the reaction mixture by GC/MS (Scheme 4).

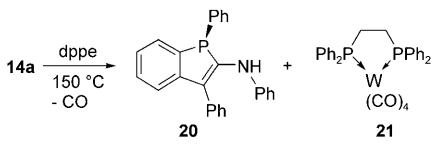


Scheme 3.



Scheme 4.

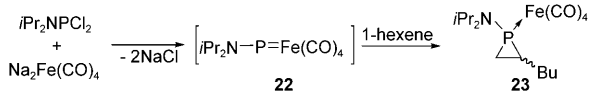
Demetallation: In view of the current increasing interest in unsaturated phosphorus ligands in homogenous catalysis,[30] we focussed our attention to the demetallation of the novel 2-aminophosphindoles. Heating W(CO)$_5$-complexed **14a**, as a test-case, with (Ph$_2$PCH$_2$)$_2$ (dppe) in refluxing xylene[31] yielded the free phosphindole **20** as the sole product together with [(dppe)W(CO)$_4$] complex **21** (Scheme 5).



Scheme 5. Synthesis of free phosphindole **20**.

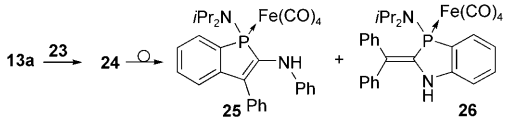
Product **20** was purified by column chromatography and could be isolated as a yellow solid in 84% yield. The removal of the [W(CO)$_5$] group is clearly reflected in the ^{31}P NMR features; its δ(^{31}P) at −7.4 ppm shows the expected shielding on demetallation which is in accordance with the parent 1-phenyl-phosphindole.[32] While **14a** has sizable ^1J(C,P) couplings of 46.6 (P,C$_1$) and 52.8 Hz (P,C$_8$), the free phosphine **20** displays much smaller ^1J(C,P) couplings of 6.8 and 1.8 Hz, respectively, which resembles that for the 3,4-dimethyl-1-phenyl-1*H*-phosphole (^1J(C,P) = 43.6 Hz,[33,34] versus 4.0 Hz[35]).

Identification of the intermediate: Lower reaction temperatures are needed in order to detect an intermediate in the formation of the 2-aminophosphindoles **14**, which is possible with iron complexed phosphinidene [*i*Pr$_2$N-P=Fe(CO)$_4$] (**22**). This reagent is generated in 1-hexene by condensation of an aminodichlorophosphane with Collman's reagent, [Na$_2$Fe(CO)$_4$]. In this solvent it is trapped as phosphirane **23**, which is an effective reservoir of **22**, as illustrated by its quantitatively transfer to alkynes to give phosphirenes at ambient temperatures (Scheme 6).[36,37]



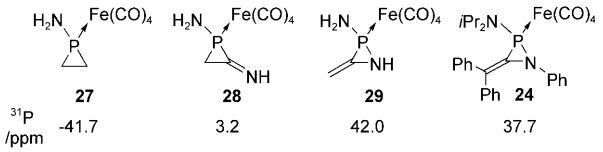
Scheme 6.

Monitoring by ^{31}P NMR the reaction of a 1-hexene solution of **23** (0.1 M) with **13a** at room temperature did show the appearance of a single intermediate (37.7 ppm, 5%, 6 h), which, unfortunately, was not amenable to isolation. Performing the reaction at the slightly elevated temperature of 40°C gave two isolated products in a 1:1 ratio, expected 2-aminophosphindole **25** (δ^{31}P 112.3, 29%) with NMR features similar to **14** and a characteristic NH group (δ^1H 5.9, ^3J(H,P) = 4.6 Hz), and novel 1*H*-benzo[1,3]azaphosphole **26** (δ^{31}P 104.2, 29%) (Scheme 7). Interestingly, the ratio of **25** to **26** is temperature-dependent (30°C, 2:1; 70°C, 1:5). The assignment of **26** is based on multinuclear NMR spectra and NOE experiments showing N*H* hydrogen interactions with the *ortho*-hydrogens of the benzannelated ring and one of the phenyl groups.



Scheme 7.

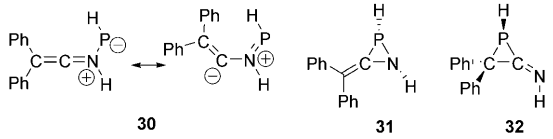
To establish the nature of intermediate **24** and presuming it to originate from addition of the phosphinidene to either the C=C or C=N bond of the ketenimine, we calculated with



density functional theory the ^{31}P NMR chemical shifts of model compounds **28** and **29** in comparison to parent **27**.[38]

The calculated ^{31}P NMR chemical shift for **27** (−41.7) is in excellent agreement with those observed experimentally (δ^{31}P −39 to −47) for diisopropylamino-substituted $Fe(CO)_4$-complexed phosphiranes.[37] Introducing an exocyclic imine **28** gives an upfield shift, but the calculated chemical shift (3.2 ppm) doesn't compare with that observed for the intermediate (δ^{31}P 37.7) in contrast to that of **29** (42.0 ppm). Therefore, we assume that the intermediate is methylene-azaphosphirane **24**.[39]

Mechanism: Two questions remain. How can a methylene-azaphosphirane rearrange to an aminophosphindole and why does an additional product result with the *i*Pr_2N-P=$Fe(CO)_4$ phosphinidene. These questions are addressed at the (U)B3LYP/6-31G* level of theory. To keep the calculations manageable model structures are used without the transition metal group, without the substituent on the ketenimine nitrogen, and with the phosphorus carrying either a hydrogen or an amino group.[40]



Three approaches of singlet phosphinidene ^{1}PH to the ketenimine are feasible, that is, to the nitrogen lone pair to give P,N-ylide **30**, addition to the C=N bond forming alkylidene-azaphosphirane **31**, and C=C bond addition resulting in phosphirane-2-ylideneamine **32**. The reaction energies leading to these three minima are 48.3, 68.4, and 66.0 kcal mol^{-1}, respectively.[41] While P,N-ylide **30**, non-planar (ΔE = 4.9 kcal mol^{-1}) and bent ($\sphericalangle$CCN 146.4°) due to resonance stabilization, is by far the least stable of the three it is likely the initial (kinetic) product to then convert to **31** with a barrier of 10.8 kcal mol^{-1} (Figure 2).[42]

Starting from methylene-azaphosphirane **31**, a direct conversion into 1,7-dihydrophosphindol-2-ylideneamine **33** was found, in which the empty p orbital of the phosphorus atom attacks the π system of the nearby phenyl group, corresponding to a concerted (closed-shell) [1,5]-sigmatropic shift that requires 24.6 kcal mol^{-1} and is exothermic by 2.8 kcal mol^{-1} (Figure 3). The associated transition structure **TS31–33**, confirmed by an IRC calculation, has P1–C4 and P1–N1 distances of 2.579 and 2.319 Å, respectively, which

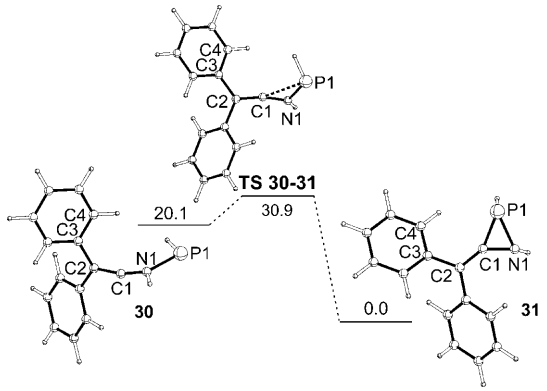


Figure 2. Relative B3LYP/6-31G* energies [kcal mol^{-1}] for the conversion of P,N-ylide **30** to methylene-azaphosphirane **31**. Selected bond lengths [Å] and angles [°] of **30**: P1–N1 1.795, C1–N1 1.277, C1–C2 1.321, C2-C1-N1 146.4; **TS30–31**: P1–C1 2.506, P1–N1 1.835, C1–N1 1.270, C1–C2 1.328; **31**: P1–C1 1.809, P1–N1 1.823, C1–N1 1.389, C1–C2 1.343, C1-P1-N1 45.0.

are in agreement with a pericyclic Woodward–Hoffmann "allowed" concerted antarafacial[1,5]-sigmatropic shift.[43] In addition, starting from phosphirane-2-ylideneamine **32**, a direct conversion into **33** with inversion of the phosphorus center was found as well, representing a concerted (closed-shell) [1,3]-sigmatropic shift that requires 20.5 kcal mol^{-1} and is exothermic by 5.3 kcal mol^{-1} (Figure 3). The associated transition structure **TS32–33** has P1–C2 and P1–C4 distances of 2.681 and 2.704 Å, respectively, which are in the expected bonding range for a Woodward–Hoffmann "allowed" concerted suprafacial [1,3]-sigmatropic shift.[10] Both of these rearrangements can be considered, at least formally, as an *intra*-molecular electrophilic aromatic substitution with replacement of an *ortho* hydrogen from the phenyl group for a phosphorus obtaining Wheland intermediate **33**.[44] However, both rearrangements are unusual. While the [1,3]-sigmatropic shift of vinylphosphiranes into phospholenes is experimentally ascertained,[45,46] there is scant precedent for this type of rearrangement with aromatics.[47] In addition, the [1,5]-sigmatropic phosphirane–phospholene rearrangement has also been observed experimentally,[43] but no precedents are known for this rearrangement with aromatics. Expectedly, 2-aminophosphindole **34** is the global minimum and can be formed directly from **33** via a hydrogen shift to nitrogen[48] with an exothermicity of 31.4 kcal mol^{-1}; its bond lengths are in good agreement with those experimentally ascertained for compound **16a** in the crystal.

The special reactivity of alkylidenephosphiranes is induced by its exocyclic double bond, which increases the strain energy by 6.8 kcal mol^{-1}, as was calculated for the parent C_3H_5P at the G3(MP2) level of theory,[8] and makes the heterocyclic ring more prone to rearrangement. Indeed, by removing the exocyclic double bond in model compound **32** the concerted [1,3]-sigmatropic shift becomes unfavorable with an endothermicity of 11.8 kcal mol^{-1} and with a reaction barrier that increases by 18.1 to 38.6 kcal mol^{-1} at the B3LYP/6-31G* level of theory.

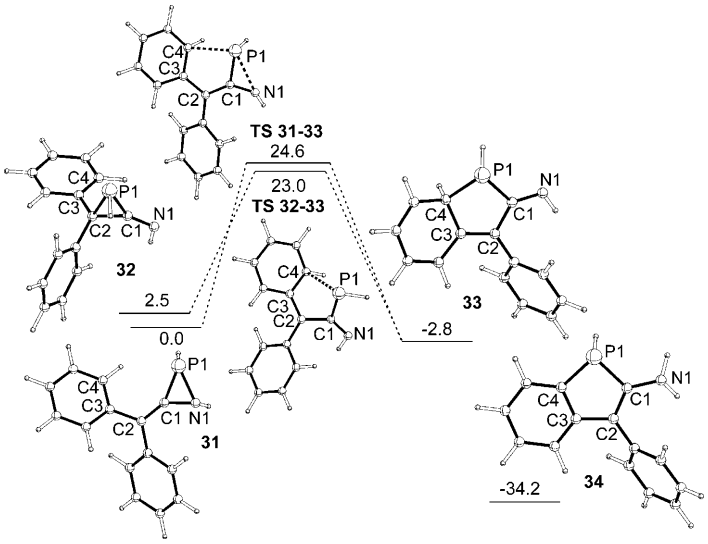
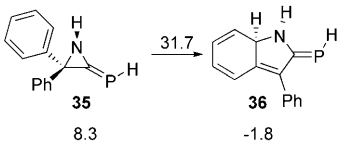


Figure 3. Relative B3LYP/6-31G* energies [kcal mol^{-1}] for the rearrangement of **31** and **32** into **33**. Selected bond lengths [Å] and angles [°] of **32**: P1−C1 1.836, P1−C2 1.975, C1−N1 1.261, C1−C2 1.479, C1-P1-C2 45.5; **TS31–33**: P1−C1 1.801, P1−C4 2.579, P1−N1 2.319, C1−N1 1.322, C1−C2 1.400; **TS32–33**: P1−C1 1.840, P1−C2 2.681, P1−C4 2.704, C1−N1 1.291, C1−C2 1.489; **33**: C1−N1 1.280, C1−C2 1.481, C2−C3 1.371; **34**: P1−C1 1.848, P1−C4 1.831, C1−N1 1.384, C1−C2 1.370, C2−C3 1.471, C1-P1-C4 89.3.

To elaborate on all valence isomers of methylene-azaphosphirane **31**, we also explored the rearrangement of 2-phosphanylidene-aziridine **35** into dihydro-1*H*-indole **36**. Aziridine **35**, which is less stable than **31** by 8.3 kcal mol^{-1} due to its more strained ring structure[49] and exocyclic C=P double bond,[7a] can indeed undergo an exothermic (ΔE = − 10.1 kcal mol^{-1}) concerted (closed-shell) [1,3]-sigmatropic shift to **36** with inversion of the nitrogen center, albeit that the barrier of 31.7 kcal mol^{-1} is sizeable (Scheme 8).[50]



Scheme 8.

On the basis of these DFT calculations, phosphirane-2-ylideneamine **32** cannot be excluded as intermediate in the formation of 2-aminophosphindole **34**, since it bears a comparable stability (ΔE = 2.5 kcal mol^{-1}) to methylene-azaphosphirane **31**.[51] More importantly, both transitions, **TS31–33** and **TS32–33**, have similar energies and similar geometries at the B3LYP/6-31G* level of theory. Without bulky, stabilizing substituents, alkylidenephosphiranes are known to undergo [1,3]-shifts seemingly with diradical character,[5,8,12] that raises the question whether **TS31–33** and **TS32–33** are not identical at the unrestricted level of theory. Indeed, at the UB3LYP/6-31G*, using a spin-projection method to obtain proper open-shell singlet energies,[52] the open-shell transition structure **37** ($\Delta E^{\neq}$ = 22.6 kcal mol^{-1}) was found together with **38** ($\Delta E^{\neq}$ = 27.8 kca mol^{-1}, Figure 4),[53] which

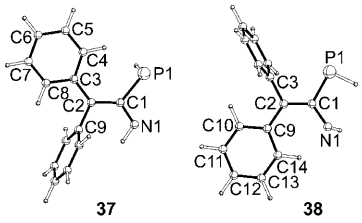
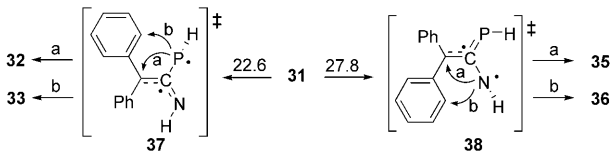


Figure 4. Open-shell transition states **37** and **38** (UB3LYP/6-31G*). Selected bond lengths [Å] and angles [°] of **37**: P1−C1 1.877, C1−N1 1.304, C1−C2 1.457, C2−C3 1.450, C2−C9 1.501, C3−C4 1.421, P1-C1-C2-C3 1.0, C1-C2-C3-C4 1.1; **38**: P1−C1 1.806, C1−N1 1.387, C1−C2 1.397, C2−C3 1.500, C2−C9 1.469, P1-C1-C2-C9 0.4, C1-C2-C9-C14 5.0.

are the heteroatom analogues[5b] of the well-known trimethylenemethane (TMM) diradical intermediates for the interconversion of methylenecyclopropanes.[54,55] The B3LYP DFT method is capable of relatively economical direct comparisons of concerted and diradical mechanisms and is favored over the computational demanding multiconfiguration approach.[10,52]

The N/P-allyl-radical moieties of **37** and **38** are resonance stabilized through conjugation with a phenyl substituent,[56] thereby inducing radical character on the aromatic ring carbons. As a result, rearrangement to bicyclic **33** and **36** becomes possible besides formation of alkylidene-heterocyclopropanes **32** and **35**, respectively (Scheme 9). Interestingly,



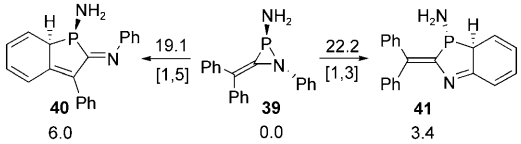
Scheme 9.

both diradical-like transition structures are favored over the corresponding concerted pathways (**TS31–33** and **TS35–36**), by ~2 to 4 kcal mol^{-1}, respectively. Therefore, the energetically most favorable process starting from azaphosphirane **31** is the diradical-like rearrangement via **37** to phosphirane **32** or phospholene **33**, with the 2-aminophosphindole **34** as the thermodynamic sink after a proton shift from **33**. The connection of open-shell transition state **38** to azaphosphirane **31** was confirmed by an IRC calculation, while tracing the IRC of **37** and **38** in all other directions was hampered by the near zero slope of the potential energy surface.

The question remains why two different products are formed by using the amino-substituted phosphinidene **22**. To address this issue we expanded the model system with a phenyl group on the nitrogen atom and an amino group on

the phosphorus atom. The donating amino-substituent notably changes the characteristics of the rearrangements, favoring closed-shell pericyclic mechanisms over open-shell pathways (Figure 5).[57]

As starting point we use again the kinetic product, methylene-azaphosphirane **39**, that is formed on addition of the phosphinidene to the C=N bond of the ketenimine. From **39** two reaction pathways are considered. Formation of 2-aminophosphindole **25** can be modeled to result from a concerted [1,5]-sigmatropic shift (**39** → **40**; see Scheme 10)[58] followed by a H-shift (**42**), which has an overall exothermicity of 22.7 kcal mol^{-1}. The first step of this process is 6.0 kcal mol^{-1} endothermic and has a barrier (**TS39–40**) of 19.1 kcal mol^{-1} that is 5.5 kcal mol^{-1} less than for the **31** → **33** conversion. The lower barrier can be attributed to electron donation of the amino substituent, which is reflected by its planarity and the short P1–N2 bond (1.672 Å), and the stabilizing N-phenyl group. Formation of 1*H*-benzo-[1,3]azaphosphole **26** can be modeled to result from a concerted [1,3]-sigmatropic shift (**39** → **41**), which is unprecedented for an azaphosphirane, followed by a H-shift (**43**) with an overall exothermicity of 23.7 kcal mol^{-1}. The first step of this process is slightly endothermic (3.4 kcal mol^{-1}) with a barrier (**TS39–41**) of 22.2 kcal mol^{-1} that is only slightly higher than that of the [1,5]-shift illustrating the same influence of the substituents (planar amino substituent; *d*-(P1–N2) 1.672 Å). For completeness, we note that the initial "[1,5]-product" **40** can rearrange (closed-shell) to the initial "[1,3]-product" **41′**, prior to a H-shift, with a barrier of 15.2 kcal mol^{-1} (Figure 6). The preference for the formation of **25** at 30 °C in the experiment is reflected in the lower barrier for the conversion **39**→**40** (kinetic) compared to **39**→**41**; whereas at 70 °C, **26** is favored due to the more stable **41** (thermodynamic).



Scheme 10.

Next, the absence of a 1*H*-benzo[1,3]azaphosphole similar to **26** in the reaction of the phosphinidenes R-P=W(CO)$_5$ (R = Ph, Me) with ketenimines was substantiated by calculations on the model system shown in Figure 5 by using PH instead of PNH$_2$ derivatives. The energies of these P-unsubstituted species are again relative to **39**(PH) and are given in parentheses. The concerted [1,5]-shift for forming the 2-aminophosphindoles ($\Delta E^{\neq}$ = 23.1 kcal mol^{-1}) is now favored over the [1,3]-shift that results in 1*H*-benzo-[1,3]azaphospholes by way of both concerted ($\Delta E^{\neq}$ = 32.2 kcal mol^{-1}) and diradical open-shell pathways ($\Delta E^{\neq}$ = 24.9 kca mol^{-1}, $\langle S^2\rangle = 0.84$), which concurs with the experiment. We note that the small energy difference between the open- and closed-shell pathways is underestimated at this level of theory.[52] Expectedly, an isomerization analogous to **TS40–41′** does not exist for the unsubstituted derivates (PH). Complexation of the phosphorus center by M(CO)$_n$ is expected to result in a stabilization of the reagents and products, thereby further reducing the barriers for rearrangement.[10] Unfortunately, incorporation of the transition metal fragment in these reaction pathways is currently beyond our computational means.

Conclusion

In this paper we have described the reaction of the transient electrophilic phosphinidene complexes R-P=W(CO)$_5$ with N-substituted-diphenylketenimines. Each of the ketenimines gives unexpectedly the novel 2-aminophosphindoles as sole products, as confirmed by an X-ray crystal structure for one of them. Only *N-tert*-butyl-diphenylketenimine **13c** is not selective and decomposes partly to isobutene of which its

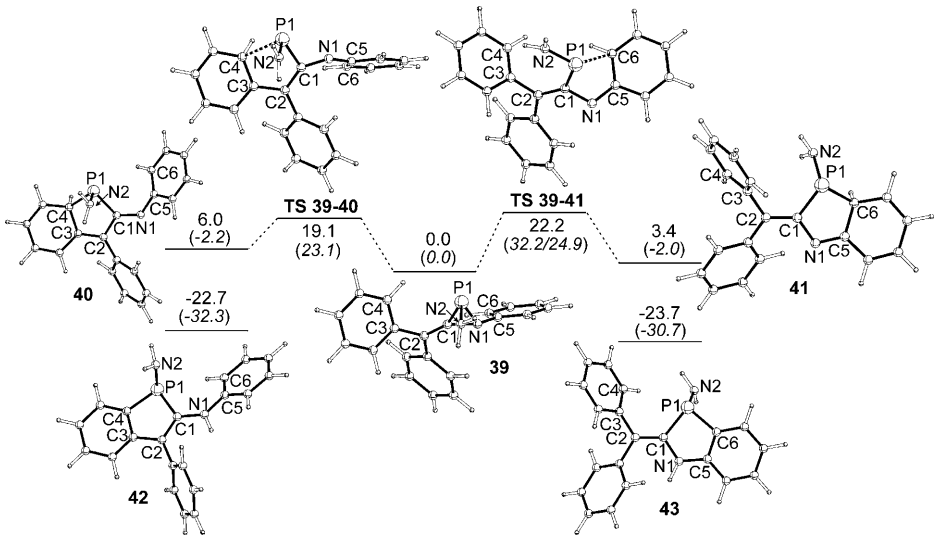


Figure 5. Relative (U)B3LYP/6-31G* energies [kcal mol^{-1}] for **39**–**43** (PNH$_2$), the relative energies [kcal mol^{-1}] for the unsubstituted derivatives (PH) are given in parentheses. Selected bond lengths [Å] and angles [°] of **39**: P1–C1 1.794, P1–N1 1.818, P1–N2 1.699, C1–N1 1.383, C1–C2 1.354, C1-P1-N1 45.0; **TS39–40**: P1–C1 1.839, P1–C4 2.471, P1–N2 1.672, C1–N1 1.320; **40**: P1–N2 1.723, C1–N1 1.283, C1–C2 1.475, C2–C3 1.376, C3–C4 1.519; **TS39–41**: P1–C1 1.834, P1–C6 2.663, P1–N2 1.672, C1–N1 1.394; **41**: P1–N2 1.725, C1–N1 1.396; **42**: P1–C1 1.860, P1–C4 1.833, P1–N2 1.721, C1–N1 1.380, C1–C2 1.373; **43**: P1–C1 1.892, P1–C6 1.835, P1–N2 1.729, C1–N1 1.394, C1–C2 1.366.

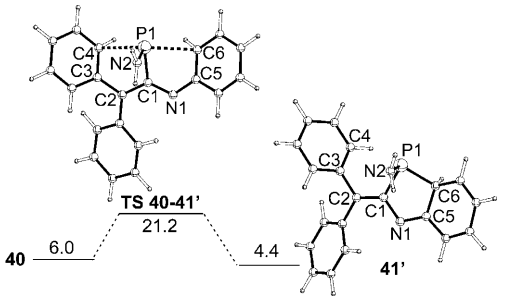


Figure 6. Relative B3LYP/6-31G* energies [kcal mol^{-1}] for the interconversion of **40** into **41′**. Selected bond lengths [Å] of **TS40–41′**: P1–C1 1.927, P1–C4 2.563, P1–C6 2.620, P1–N2 1.676, C1–N1 1.327, C1–C2 1.410, C2–C3 1.453, C5–N1 1.361.

phosphinidene addition product was isolated. No intermediates could be detected during the formation of the 2-aminophosphindoles by ^{31}P NMR spectroscopy. In contrast, experimental evidence for a methylene-azaphosphirane intermediate was found by reacting the iron-complexed phosphinidene iPr$_2$N-P=Fe(CO)$_4$ with N-phenyl-diphenylketenimine that affords the 2-aminophosphindole together with the novel methylene-2,3-dihydro-1*H*-benzo[1,3]azaphosphole. Theoretical calculations at the (U)B3LYP/6-31G* level of theory suggest that both products result from the initially formed methylene-azaphosphirane by, respectively, a [1,5]- or [1,3]-sigmatropic rearrangement followed by a H-shift. Both of these rearrangements are unusual and are facilitated by the exocyclic double bond that causes the intermediate azaphosphirane to be more strained. In agreement with the experimental observations, these remarkably selective conversions can be tuned by changing the substituents, where, an amino substituent on phosphorus stabilizes the formation of the 1*H*-benzo[1,3]azaphosphole.

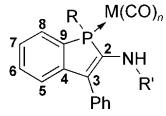
Experimental Section

Computations: All electronic structure calculations were performed using the GAUSSIAN 98 suite of programs (G98).[59] Becke's three-parameter hybrid exchange functional[60] combined with the Lee–Yang–Parr correlation functional,[61] denoted as B3LYP, and the 6-31G* basis set was used for the density functional theory (DFT) calculations. First and second order energy derivatives were computed to confirm that minima or transition structures had been located. Intrinsic reaction coordinate driving calculations (IRC) were performed to establish connections between transition structures and minima. To extract the open-shell singlet energies from the mixture of singlet and triplet states that are obtained on calculating open-shell singlet energies with spin unrestricted DFT, we applied the spin-projection method by Houk and co-workers.[52]

The NMR calculations were performed using the Amsterdam density functional (ADF) package 2002.03.[62] In the geometry optimizations all atoms were described by a triple-ξ basis set with polarization functions, corresponding to the TZP basis set in ADF. The 1s core shell of carbon, nitrogen and oxygen and the 1s^{2}2p core shells of phosphorus were treated by the frozen core approximation. The metal center (Fe) was described by a triple-ξ basis set for the outer *ns*, *np*, *nd* and (n+1)s orbitals, whereas the shells of lower energy were treated by the frozen core approximation. All calculations were performed at the nonlocal exchange self-consistent field (NL-SCF) level, using the local density approximation (LDA) in the Vosko–Wilk–Nusair parameterization[63] with nonlocal corrections for exchange (Becke88)[60] and correlation (Perdew86).[64] All geometries were optimized by using the analytical gradient method implemented by Versluis and Ziegler,[65] including relativistic effects by the zero-order regular approximations (ZORA).[66] The ^{31}P NMR chemical shift tensors were calculated with ADF's NMR program,[67] with an all-electron basis set for the phosphorus atoms. The total isotropic shielding tensors were referenced against PMe_3, which has a value of 353.5 and an experimental chemical shift at $\delta^{31}P = -62$ with respect to 85% H_3PO_4.

General: All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (298 K) on a Bruker Advance 250 (^{1}H, ^{13}C and ^{31}P) and MSL 400 (^{1}H, ^{13}C), internally referenced to residual solvent resonances (^{1}H: δ 7.25 ppm, ^{13}C{^{1}H}: 77.0 ppm ($CDCl_3$) and ^{1}H: δ 7.15 ppm, ^{13}C{^{1}H}: 128.0 ppm (C_6D_6) or using 85% H_3PO_4 (^{31}P) as external standard. High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 and IR spectra on a Mattson-6030 Galaxy spectrophotometer. Elemental analysis was obtained from Mikroanalytisches Labor Pascher, in Remagen-Bandorf (Germany). Melting points were measured on samples in unsealed capillaries and are uncorrected.

Complexes **12a** and **12b** were prepared according to a procedure by Mathey et al.[21] *N*-Phenyl-diphenylketenimine **13a**,[68] *N*-isopropyl-diphenylketenimine **13b**,[69] *N-tert*-butyl-diphenylketenimine **13c**,[69] *N,N′*-bis(diphenylethenylidene)-1,4-benzenediamine **15**[70] and complex **23**[37] were synthesized according to literature procedures. The general structure of the aminophosphindole product is shown below with numbered carbon atoms.



(1,3-Diphenyl-2-phenylamino-1*H*-phosphindole)pentacarbonyltungsten (14a): Complex **12a** (0.45 g, 0.69 mmol), *N*-phenyl-diphenylketenimine (**13a**) (0.24 g, 0.90 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 8 h. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9:1) gave **14a** (0.44 g, 91%) as a pale yellow solid. Recrystallization from hexane/CH_2Cl_2 at 0 °C afforded yellow crystals. M.p. 170–171 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 17.4 ppm (^1J(P,W) = 232.7 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 119.4 (s; *o*-PhN), 121.8 (d, ^3J(C,P) = 4.9 Hz; C_5), 122.0 (s; *p*-PhN), 125.9 (d, ^3J(C,P) = 10.3 Hz; C_7), 128.2 (s; *p*-PhC_3), 128.6 (d, ^2J(C,P) = 23.9 Hz; C_3), 128.7 (s; *m*-PhN), 128.7 (d, ^2J(C,P) = 16.1 Hz; C_8), 129.2 (d, ^3J(C,P) = 10.6 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.5 (s; *o*-PhC_3), 130.5 (d, ^4J(C,P) = 1.3 Hz; C_6), 131.4 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 132.7 (d, ^1J(C,P) = 36.3 Hz; *ipso*-PhP), 132.8 (d, ^2J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^3J(C,P) = 7.5 Hz; *ipso*-PhC_3), 138.1 (d, ^1J(C,P) = 52.8 Hz; C_9), 141.3 (d, ^3J(C,P) = 1.5 Hz; *ipso*-PhN), 143.7 (d, ^2J(C,P) = 8.7 Hz; C_4), 145.3 (d, ^1J(C,P) = 46.6 Hz; C_2), 195.9 (d, ^2J(C,P) = 6.7 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 197.9 ppm (d, ^2J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.87 (d, ^3J(H,P) = 12.1 Hz, 1H; N*H*), 6.37–6.40 (m, 2H; *o*-Ph*H*N), 6.73–6.77 (m, 1H; *p*-Ph*H*N), 6.83–6.88 (m, 2H; *m*-Ph*H*N), 7.21–7.27 (m, 2H; C_5H, C_7H), 7.31–7.48 (m, 10H; Ph*H*), 7.52–7.58 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): $\tilde{\nu}$ = 1913, 1929 (s/br, C=O$_{eq}$), 2072 (m, C=O$_{ax}$); HR-MS (EI, 70 eV): *m/z* (%): 701 (10) [*M*]$^+$, 617 (26) [*M* −3CO]$^+$, 561 (32) [*M*−5CO]$^+$, 377 (100) [*M*−W(CO)$_5$]$^+$; *m/z*: calcd for $C_{31}H_{20}O_5NP^{184}W$: 701.05890; found: 701.060227; elemental analysis calcd (%): C 53.09, H 2.87; found: C 53.15, H 2.93.

(1,3-Diphenyl-2-isopropylamino-1*H*-phosphindole)pentacarbonyltungsten (14b): Complex **12a** (0.26 g, 0.39 mmol), *N*-isopropyl-diphenylketenimine (**13b**) (0.12 g, 0.51 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (2.5 mL) at 55 °C for 11 h. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9:1) gave **14b** (0.12 g, 46%) as a pale yellow solid. Recrystallization from pentane at 0 °C afforded yellow crystals. M.p. 127–128 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 12.9 ppm (^1J(P,W) = 230.4 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 23.4 (s; CH_3), 23.9 (s; CH_3), 48.6 (d, ^3J(C,P) = 5.0 Hz; $CH(CH_3)_2$), 118.5 (d, ^2J(C,P) = 15.2 Hz; C_3), 120.1 (d, ^3J(C,P) = 5.2 Hz; C_5), 123.8 (d, ^3J(C,P) = 10.7 Hz; C_7), 127.7 (s; *p*-PhC_3),

128.6 (d, ^2J(C,P) = 14.9 Hz; C_8), 129.1 (d, ^3J(C,P) = 10.4 Hz; *m*-PhP), 129.3 (s; *m*-PhC_3), 129.8 (s; *o*-PhC_3), 130.6 (d, ^4J(C,P) = 1.2 Hz; C_6), 130.8 (d, ^1J(C,P) = 36.0 Hz; *ipso*-PhP), 131.4 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 133.1 (d, ^2J(C,P) = 13.6 Hz; *o*-PhP), 134.6 (d, ^3J(C,P) = 7.5 Hz; *ipso*-PhC_3), 136.8 (d, ^1J(C,P) = 54.4 Hz; C_9), 146.1 (d, ^2J(C,P) = 9.4 Hz; C_4), 151.6 (d, ^1J-(C,P) = 51.3 Hz; C_2), 196.2 (d, ^2J(C,P) = 6.7 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 198.1 ppm (d, ^2J(C,P) = 21.3 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.46 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3), 0.99 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3), 3.29–3.39 (m, 1H; $CH(CH_3)_2$), 3.78 (dd, ^3J(H,H) = 10.5 Hz, ^3J(H,P) = 19.9 Hz, 1H; N*H*), 6.98–7.01 (m, 1H; C_5H), 7.06–7.12 (m, 1H; C_7H), 7.23–7.28 (m, 1H; C_6H), 7.30–7.35 (m, 1H; C_8H), 7.37–7.48 (m, 6H; *m*-Ph*H*P, *p*-Ph*H*P, *m*-PhHC_3, *p*-PhHC_3), 7.49–7.54 (m, 2H; *o*-PhHC_3), 7.61–7.67 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): $\tilde{\nu}$ = 1915, 1929 (s/br, C=O_{eq}), 1987 (m, C=O_{eq}), 2072 (m, C=O_{ax}); HR-MS (EI, 70 eV): *m*/*z* (%): 667 (24) $[M]^+$, 611 (40) $[M-2CO]^+$, 527 (58) $[M-5CO]^+$, 343 (100) $[M-W(CO)_5]^+$; *m*/*z*: calcd for $C_{28}H_{22}NO_5P^{184}W$: 667.07458; found: 667.07747.

(1,3-Diphenyl-2-*tert*-butylamino-1*H*-phosphindole)pentacarbonyltungsten (14c): Complex **12a** (84.7 mg, 129.4 μmol), *N*-*tert*-butyl-diphenylketenimine (**13c**) (35.5 mg, 142.4 μmol) and 1 mg CuCl (10 μmol) were heated in toluene (0.7 mL) at 55 °C for 7 h generating 39 % of **14c** and 19 % of **17**[25] (^{31}P NMR yields). Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (19:1) gave **14c** (34.0 mg, 39 %) as a pale yellow solid and **17**[25] (8.3 mg, 13 %) as a colorless solid. Recrystallization of **14c** from pentane/CH_2Cl_2 at −20 °C afforded yellow crystals. GC-MS analysis of the reaction mixture showed the presence of diphenylacetonitrile. M.p. 164 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 19.0 ppm (^1J(P,W) = 234.0 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 30.4 (s; C(CH_3)$_3$), 53.6 (s; $C(CH_3)_3$), 121.5 (d, ^3J(C,P) = 4.8 Hz; C_5), 125.6 (d, ^3J(C,P) = 9.9 Hz; C_7), 128.1 (s; *p*-PhC_3), 128.2 (d, ^2J(C,P) = 13.2 Hz; C_8), 128.9 (d, ^3J(C,P) = 10.4 Hz; *m*-PhP), 129.3 (s; *m*-PhC_3), 130.1 (s; *o*-PhC_3), 130.2 (d, ^4J(C,P) = 1.3 Hz; C_6), 130.3 (d, ^2J(C,P) = 19 Hz; C_3), 131.1 (d, ^1J(C,P) = 35.3 Hz; *ipso*-PhP), 131.4 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 133.5 (d, ^2J(C,P) = 13.0 Hz; *o*-PhP), 135.0 (d, ^3J-(C,P) = 7.3 Hz; *ipso*-PhC_3), 140.2 (d, ^1J(C,P) = 53.1 Hz; C_9), 143.9 (d, ^2J-(C,P) = 9.3 Hz; C_4), 150.9 (d, ^1J(C,P) = 47.2 Hz; C_2), 196.6 (d, ^2J(C,P) = 6.6 Hz, ^1J(C,W) = 125.9 Hz; *cis*-CO), 198.3 ppm (d, ^2J(C,P) = 21.9 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.87 (s, 9H; CH_3), 3.71 (d, ^3J(H,P) = 22.5 Hz, 1H; N*H*), 6.93–6.96 (m, 1H; C_5H), 7.14–7.18 (m, 1H; C_7H), 7.22–7.30 (m, 2H; C_6H, C_8H), 7.35–7.40 (m, 2H; *o*-PhHC_3), 7.40–7.50 (m, 4H; *m*-Ph*H*P, *p*-Ph*H*P, *p*-PhHC_3), 7.52–7.56 (m, 2H; *m*-PhHC_3), 7.59–7.66 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): $\tilde{\nu}$ = 1942 (s/br, C=O_{eq}), 1985 (m, C=O_{eq}), 2072 (m, C=O_{ax}); HR-MS (EI, 70 eV): *m*/*z* (%): 681 (15) $[M]^+$, 625 (15) $[M-2CO]^+$, 597 (1) $[M-3CO]^+$, 569 (4) $[M-4CO]^+$, 541 (19) $[M-5CO]^+$, 483 (25) $[M-5CO-t\mathrm{Bu}]^+$, 357 (100) $[M-W(CO)_5]^+$; *m*/*z*: calcd for $C_{29}H_{24}NO_5P^{184}W$: 681.08790; found: 681.09021; elemental analysis calcd (%): C 51.12, H 3.55; found: C 51.10, H 3.57.

(1-Methyl-2-phenylamino-3-phenyl-1*H*-phosphindole)pentacarbonyltungsten (14d): Complex **12b** (0.29 g, 0.49 mmol) and *N*-phenyl-diphenylketenimine (**13a**) (0.20 g, 0.74 mmol) were heated in refluxing toluene (4 mL) for 11.5 h. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9:1) gave **14d** (0.17 g, 54 %) as a pale yellow solid. Recrystallization from hexane/CH_2Cl_2 at 0 °C afforded yellow crystals. M.p. 193 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 3.0 ppm (^1J(P,W) = 226.3 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 22.0 (d, ^1J(C,P) = 22.5 Hz; CH_3), 119.7 (s; *o*-PhN), 122.3 (d, ^3J(C,P) = 4.9 Hz; C_5), 122.7 (s; *p*-PhN), 126.1 (d, ^3J(C,P) = 10.0 Hz; C_7), 127.8 (d, ^2J(C,P) = 13.4 Hz; C_8), 128.3 (s; *p*-PhC_3), 129.1 (s; *m*-PhN, *m*-PhC_3), 129.3 (s; *o*-PhC_3), 130.5 (d, ^4J(C,P) = 1.5 Hz; C_6), 131.5 (d, ^2J(C,P) = 18.3 Hz; C_3), 133.7 (d, ^3J(C,P) = 7.0 Hz; *ipso*-PhC_3), 137.1 (d, ^1J(C,P) = 50.6 Hz; C_9), 142.3 (d, ^3J(C,P) = 1.2 Hz; *ipso*-PhN), 143.2 (d, ^2J(C,P) = 8.9 Hz; C_4), 144.0 (d, ^1J(C,P) = 47.1 Hz; C_2), 196.1 (d, ^2J(C,P) = 6.8 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 198.7 ppm (d, ^2J(C,P) = 20.6 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.07 (d, ^2J(H,P) = 8.0 Hz, 3H; CH_3), 5.75 (d, ^3J(H,P) = 11.4 Hz, 1H; N*H*), 6.86–6.89 (m, 2H; *o*-Ph*H*N), 6.95–6.99 (m, 1H; *p*-Ph*H*N), 7.19–7.27 (m, 3H; *m*-Ph*H*N, C_5H), 7.31–7.47 (m, 7H; C_6H, C_7H, PhHC_2), 7.57–7.62 ppm (m, 1H; C_8H); HR-MS (EI, 70 eV): *m*/*z* (%): 639 (18) $[M]^+$, 555 (43) $[M-3CO]^+$, 483 (35) $[M-5CO-Me]^+$, 315 (100) $[M-W(CO)_5]^+$; *m*/*z*: calcd for $C_{26}H_{18}O_5NP^{184}W$: 639.04327; found: 639.040753; IR (KBr): $\tilde{\nu}$ = 1921, 1942 (s/br, C=O_{eq}), 1977 (m, C=O_{eq}), 2070 (m, C=O_{ax}).

(*N*,*N*′-Bis-1,3-diphenyl-1*H*-phosphindol-2-yl-1,4-phenylenediamine)pentacarbonyl tungsten (16): Complex **12a** (0.66 g, 1.01 mmol) and *N*,*N*′-bis(diphenylethenylidene)-1,4-phenylenediamine (**15**) (0.21 g, 0.46 mmol) were heated in refluxing toluene (8 mL) for 14 h. Complex **16b** precipitated as a yellow solid (0.13 g, 21 %). The extract was evaporated to dryness and the residue was chromatographed over neutral aluminum oxide with pentane/dichloromethane (4:1) to give complex **16a** (0.17 g, 28 %) as a pale yellow solid. Recrystallization from hexane/CH_2Cl_2 at 0 °C afforded yellow crystals of **16a**. (*R*,*R*) and (*S*,*S*): m.p. 237 °C (decomp.); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 16.5 ppm (^1J(P,W) = 232.8 Hz); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 120.3 (s; *o*-PhN), 121.5 (d, ^3J(C,P) = 4.9 Hz; C_5), 125.7 (d, ^3J(C,P) = 10.3 Hz; C_7), 127.6 (d, ^2J(C,P) = 16.3 Hz; C_3), 128.2 (s; *p*-PhC_3), 128.7 (d, ^2J(C,P) = 14.0 Hz; C_8), 129.1 (d, ^3J(C,P) = 10.5 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.5 (s; *o*-PhC_3), 130.5 (d, ^4J(C,P) = 1.3 Hz; C_6), 131.3 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 132.3 (d, ^1J(C,P) = 36.1 Hz; *ipso*-PhP), 132.7 (d, ^2J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^3J-(C,P) = 6.9 Hz; *ipso*-PhC_3), 136.3 (d, ^3J(C,P) = 1.5 Hz; *ipso*-PhN), 137.9 (d, ^1J(C,P) = 52.8 Hz; C_9), 143.8 (d, ^2J(C,P) = 8.7 Hz; C_4), 145.6 (d, ^1J-(C,P) = 47.1 Hz; C_2), 195.8 (d, ^2J(C,P) = 6.7 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 198.0 ppm (d, ^2J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (250.1 MHz,$CDCl_3$): δ = 5.63 (d, ^3J(H,P) = 13.5 Hz, 2H; N*H*), 5.92 (s, 4H; Ph*H*N), 7.15–7.24 (m, 4H; C_5H, C_7H), 7.27–7.49 ppm (m, 24H; Ph*H*); IR (KBr): $\tilde{\nu}$ = 1933 (s/br, C=O_{eq}), 1985 (m, C=O_{eq}), 2072 (s, CO_{ax}); elemental analysis calcd (%) for $C_{56}H_{34}N_2O_{10}P_2W_2$: C 50.78, H 2.59; found: C 50.47, H 2.61.

Compound 16b (*meso*): m.p. 190 °C (decomp.); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 16.3 ppm (^1J(P,W) = 232.5 Hz); ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 120.6 (s; *o*-PhN), 121.5 (d, ^3J(C,P) = 5.0 Hz; C_5), 125.7 (d, ^3J(C,P) = 10.3 Hz; C_7), 127.5 (d, ^2J(C,P) = 16.2 Hz; C_3), 128.2 (s; *p*-PhC_3), 128.7 (d, ^2J(C,P) = 14.2 Hz; C_8), 129.1 (d, ^3J(C,P) = 10.5 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.6 (s; *o*-PhC_3), 130.5 (d, ^4J(C,P) = 1.3 Hz; C_6), 131.3 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 132.4 (d, ^1J(C,P) = 36.4 Hz; *ipso*-PhP), 132.8 (d, ^2J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^3J(C,P) = 6.9 Hz; *ipso*-PhC_3), 136.4 (d, ^3J(C,P) = 1.6 Hz; *ipso*-PhN), 138.0 (d, ^1J(C,P) = 53.0 Hz; C_9), 143.9 (d, ^2J(C,P) = 8.7 Hz; C_4), 145.9 (d, ^1J(C,P) = 47.1 Hz; C_2), 195.8 (d, ^2J(C,P) = 6.7 Hz, ^1J(C,W) = 125.7 Hz; *cis*-CO), 198.0 ppm (d, ^2J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 5.65 (d, ^3J(H,P) = 13.5 Hz, 2H; N*H*), 5.92 (s, 4H; Ph*H*N), 7.15–7.24 (m, 4H; C_5H, C_7H), 7.27–7.53 ppm (m, 24H; Ph*H*); IR (KBr): $\tilde{\nu}$ = 1923 (s/br, C=O_{eq}), 1985 (m, C=O_{eq}), 2070 (s, C=O_{ax}).

1,3-Diphenyl-2-phenylamino-1*H*-phosphindole (20): Complex **14a** (156 mg, 0.22 mmol) and dppe (97 mg, 0.24 mmol) were stirred in refluxing xylene (8 mL) for 60 h. Evaporation to dryness and chromatography over neutral aluminum oxide with pentane/dichloromethane (4:1) gave **20** (70 mg, 84 %) as a yellow solid. M.p. 249–251 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = − 7.4 ppm; ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 118.2 (d, ^4J(C,P) = 8.3 Hz; *o*-PhN), 120.4 (d, ^3J(C,P) = 0.8 Hz; C_5), 121.3 (d, ^6J(C,P) = 0.5 Hz; *p*-PhN), 123.9 (d, ^3J(C,P) = 8.7 Hz; C_7), 126.2 (d, ^2J(C,P) = 7.5 Hz; C_3), 127.6 (s; *p*-PhC_3), 128.6 (s; C_6), 128.6 (d, ^3J (C,P) = 7.9 Hz; *m*-PhP), 129.0 (s; *m*-PhN), 129.3 (s; *o*-PhC_3), 129.3 (d, ^2J (C,P) = 23.2 Hz; C_8), 129.4 (d, ^4J(C,P) = 1.3 Hz; *p*-PhP), 129.8 (d, ^5J (C,P) = 1.5 Hz; *m*-PhC_3), 133.1 (d, ^2J(C,P) = 19.7 Hz; *o*-PhP), 134.0 (d, ^1J (C,P) = 17.1 Hz; *ipso*-PhP), 134.9 (d, ^3J(C,P) = 0.7 Hz; *ipso*-PhC_3), 136.6 (d, ^1J(C,P) = 1.8 Hz; C_9), 143.1 (s; *ipso*-PhN), 147.1 (d, ^2J(C,P) = 1.6 Hz; C_4), 148.7 ppm (d, ^1J(C,P) = 6.8 Hz; C_2); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.13 (br. d, ^3J(H,P) = 10.3 Hz, 1H; N*H*), 6.82–6.89 (m, 1H; *p*-Ph*H*N), 7.05–7.18 (m, 6H; C_5H, C_7H, *o*-Ph*H*N, *m*-Ph*H*N), 7.18–7.29 (m, 4H; C_6H, *m*-Ph*H*P, *p*-Ph*H*P), 7.31–7.36 (m, 2H; *o*-Ph*H*P), 7.36–7.42 (m, 1H; *p*-Ph*H*C), 7.45–7.55 ppm (m, 5H; C_8H, *m*-Ph*H*C, *o*-Ph*H*C); HR-MS (EI, 70 eV): *m*/*z* (%): 377 (100) $[M]^+$; *m*/*z*: calcd for $C_{26}H_{20}NP$: 377.13333; found: 377.13563.

Reaction of $Fe(CO)_4$-complexed phosphirane 23 with 13a: A 1-hexene solution of **23** (8 mL; 0.1 M, 0.8 mmol) and *N*-phenyl-diphenylketenimine (**13a**) (0.24 g, 0.88 mmol) were heated at 40 °C for 60 h. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide

with pentane/dichloromethane (9:1) gave **25** (0.13 g, 29%) and **26** (0.13 g, 29%) both as an orange oil. Recrystallization from pentane at −20°C afforded yellow crystals of **26**.

(1-diisopropylamino-2-phenylamino-3-phenyl-1*H*-phosphindole)tetracarbonyliron (25): $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): $\delta = 112.3$ ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 24.0$ (d, $^3J(C,P) = 3.2$ Hz; CH_3), 24.1 (d, $^3J(C,P) = 2.8$ Hz; CH_3), 51.6 (d, $^2J(C,P) = 5.9$ Hz; $CH(CH_3)_2$), 117.9 (s; *m*-PhN), 121.4 (s; *p*-PhN), 121.8 (d, $^3J(C,P) = 7.2$ Hz; C_5), 126.1 (d, $^3J(C,P) = 10.7$ Hz; C_7), 127.7 (s; *p*-Ph), 128.2 (d, $^2J(C,P) =$ unresolved; C_3), 128.4 (s; *o*-PhN), 128.5 (s; *m*-Ph), 128.8 (d, $^2J(C,P) = 12.7$ Hz; C_8), 129.2 (s; *o*-Ph), 131.6 (d, $^4J(C,P) = 1.8$ Hz; C_6), 134.9 (d, $^3J(C,P) = 10.0$ Hz; *ipso*-Ph), 136.1 (d, $^1J(C,P) = 60.9$ Hz; C_9), 141.1 (d, $^3J(C,P) = 5.8$ Hz; *ipso*-PhN), 141.3 (d, $^2J(C,P) = 15.0$ Hz; C_4), 142.8 (d, $^1J(C,P) = 65.0$ Hz; C_2), 213.8 ppm (d, $^2J(C,P) = 17.8$ Hz; *C*O); ^1H NMR (400.1 MHz, C_6D_6): $\delta = 1.01$ (d, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.09 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 4.05 (dsp, $^3J(H,H) = 6.9$ Hz, $^3J(H,P)$ unresolved, 2H; $CH(CH_3)_2$), 5.87 (d, $^3J(H,P) = 4.6$ Hz, 1H; N*H*), 6.53–6.61 (m, 3H; *m*- and *p*-Ph*H*N), 6.76–6.81 (m, 2H; *o*-Ph*H*N), 6.87–7.00 (m, 5H; C_6H, C_7H, *p*-Ph*H*, *m*-Ph*H*), 7.19–7.22 (m, $^3J(H,H) = 7.5$ Hz, 1H; C_5H), 7.24–7.27 (m, 2H; *o*-Ph*H*), 7.78–7.83 ppm (m, $^3J(H,H) = 6.9$ Hz, 1H; C_8H); IR (KBr): $\tilde{\nu} = 1927$, 1942 (s/br, C=O_{eq}), 1973 (m, C=O_{eq}), 2047 (s, C=O_{ax}); HR-MS (EI, 70 eV): *m*/*z* (%): 568 (1) $[M]^+$, 540 (1) $[M-CO]^+$, 512 (1) $[M-2CO]^+$, 484 (40) $[M-3CO]^+$, 456 (18) $[M-4CO]^+$, 400 (32) $[M-Fe(CO)_4]^+$, 357 (100) $[M-Fe(CO)_4-C_3H_7]^+$; *m*/*z*: calcd for $C_{30}H_{29}N_2O_4P^{56}Fe$: 568.12140; found: 568.12253.

(1-Diisopropylamino-2-diphenylmethylene-2,3-dihydro-1*H*-benzo-[1,3]azaphosphole)tetracarbonyliron (26): m.p. 86°C (decomp.); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): $\delta = 104.2$ ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 23.7$ (d, $^3J(C,P) = 3.7$ Hz; CH_3), 25.1 (d, $^3J(C,P) = 2.6$ Hz; CH_3), 52.3 (d, $^2J(C,P) = 7.6$ Hz; $CH(CH_3)_2$), 110.4 (d, $^3J(C,P) = 4.2$ Hz; C_5), 120.5 (d, $^3J(C,P) = 10.3$ Hz; C_7), 125.3 (d, $^1J(C,P) = 56.9$ Hz; C_9), 127.3 (d, $^2J(C,P)$ unresolved; CPh_2), 127.6 (s; *p*-Ph), 127.9 (s; *ipso*-Ph), 128 (unresolved; C_2), 128.1 (s; *p*-Ph), 128.4 (s; *ipso*-Ph), 128.8 (s; *m*-Ph), 129.6 (s; *m*-Ph), 129.6 (s; *o*-Ph), 130.0 (d, $^2J(C,P) = 12.1$ Hz; C_8), 131.2 (s; *o*-Ph), 132.0 (d, $^4J(C,P) = 1.5$ Hz; C_6), 143.2 (d, $^2J(C,P) = 5.6$ Hz; C_4), 213.5 ppm (d, $^2J(C,P) = 17.8$ Hz; *C*O); ^1H NMR (400.1 MHz, C_6D_6): $\delta = 1.08$ (d, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.12 (d, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 4.12 (dsp, $^3J(H,H) = 6.9$ Hz, $^3J(H,P)$ unresolved, 2H; $CH(CH_3)_2$), 5.70 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,P) = 2.9$ Hz, 1H; C_5H), 6.28 (d, $^3J(H,P) = 4.9$ Hz, 1H; N*H*), 6.63 (m, $^3J(H,H) = 7.5$ Hz, $^4J(H,P) = 3.2$ Hz, 1H; C_7H), 6.83 (m, $^3J(H,H) = 7.7$ Hz, 1H; C_6H), 7.02–7.04 (m, 1H; *p*-Ph*H*), 7.08–7.15 (m, 3H; *p*-Ph*H*, *m*-Ph*H*), 7.17–7.22 (m, 2H; *m*-Ph*H*), 7.32–7.35 (m, 2H; *o*-Ph*H*), 7.51–7.54 (m, 2H; *o*-Ph*H*), 7.85 ppm (dd, $^3J(H,H) = 7.6$ Hz, $^3J(H,P) = 7.9$ Hz, 1H; C_8H); IR (KBr): $\tilde{\nu} = 1917$, 1935 (s/br, C=O_{eq}), 1973 (m, C=O_{eq}), 2047 (s, C=O_{ax}); HR-MS (EI, 70 eV): *m*/*z* (%): 400 (20) $[M-Fe(CO)_4]^+$, 300 (100) $[M-Fe(CO)_4-N(C_3H_7)_2]^+$; *m*/*z*: calcd for $C_{26}H_{29}N_2P$ $[M-Fe(CO)_4]$: 400.20682; found: 400.20761.

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(no. 15), $a=20.4941(2)$, $b=14.7896(1)$, $c=18.3077(2)$ Å, $\beta=113.0025(5)°$, $V=5107.83(8)$ Å^3, $Z=4$, $\rho=1.722$ g cm^{-3}. 53344 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}=0.65$ Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda=0.71073$ Å) at a temperature of 150(2) K. An analytical absorption correction was applied ($\mu=4.624$ mm^{-1}, 0.30–0.52 correction range). 5861 Reflections were unique ($R_{int}=0.0580$). The structure was solved with automated Patterson Methods[71] and refined with SHELXL-97[72] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. One phenyl residue was disordered over two orientations. 366 Parameters were refined with 186 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0242/0.0535. $R1/wR2$ [all refl.]: 0.0356/0.0574. $S=1.071$. Residual electron density between −0.94 and 1.58 e Å^{-3}. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON[73] package. CCDC-264309 contains 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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