C−N Bond Insertion of a Complexed Phosphinidene into a Bis(imine) − A Novel 2,3-Sigmatropic Shift

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The electrophilic phosphinidene complex PhPW(CO)$_5$ reacts with bis(imine) **5**, possessing a single carbon spacer, to give the C−N insertion product **6**. B3LYP/6-31G* calculations indicate that this process occurs by way of a 2,3-sigmatropic shift from the initially formed phosphane ylide. The alternative, 1,3-dipolar cycloaddition, followed by ring-opening of the bicyclic structure, can be ruled out since both steps are energetically much more demanding. Ring-closure to an azaphosphirane is also less favorable than the C−N insertion, which is in agreement with the absence of such a product in the experiment.

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Introduction

Phosphane ylides are emerging as viable low-valent organophosphorus synthons. These highly reactive species are already commonly employed in the phospha Wittig reaction,[1] while their transition metal complexes are useful reagents for the synthesis of three- to eight-membered heterocycles.[2] These ylides are readily available. For example, the frequently used complexed nitrilium phosphane ylides **I** can be generated thermally[3] and photochemically[4] from 2H-azaphosphirene complexes. Reminiscently of regular ylides,[5] however, most transient P,N-ylides (**I**,[3,4,6] **II**,[7] and **III**[8]), P,O-ylides (**IV**[9]), P,S-ylides (**V**[10]), and P,P-ylides (**VI**[11]) are formed from direct interaction (or exchange) between complexed phosphinidenes RPW(CO)$_5$,[12] generated in situ, and the lone pair of the heteroatom-containing substrate.

Of the many types of reactions that these phosphane ylides can undergo, the 2,3-sigmatropic shift[13,5] has not yet been observed except for the somewhat related conversions of P,N-ylide **IIIa** into the formal C−H insertion product **1** and of P,O-ylide **IVa** into the bicyclic compound **2**. The initially formed ylides were obtained by treatment of RPW(CO)$_5$ with azobenzene[8] (Ph−N=N−Ph) and benzophenone [Ph−C(O)−Ph],[9a] respectively (Scheme 1). In this study, we provide evidence for the first 2,3-sigmatropic shift of a phosphane ylide formed from a complexed phosphinidene and a bis(imine) with a single carbon spacer. This work

extends recent studies on the formation of azaphosphiridines[7,9a] and the 1,3-dipolar cycloadditions of P,N-ylides.[6,7]
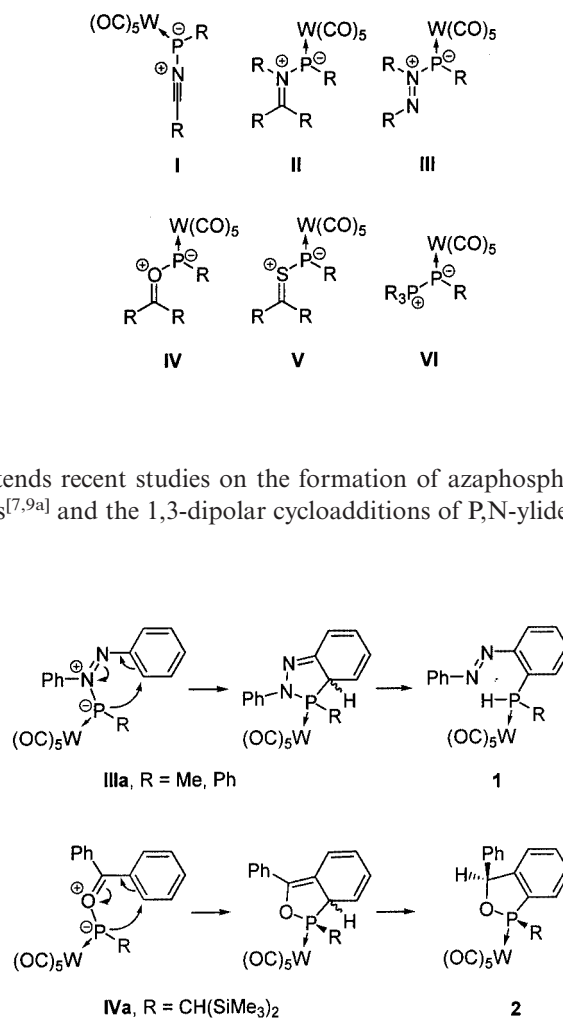

Scheme 1

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Results and Discussion

While exploring reactions between the phosphinidene complex PhPW(CO)$_5$ (**4**) − generated in situ from complex **3** at 110 °C[12,14] − and a broad range of imines, we were surprised to see this carbene-like synthon insert into a C−N single bond of bis(imine) **5**[15] to give **6** in 58% isolated yield. No 1,2-addition product could be detected in the reaction mixture.
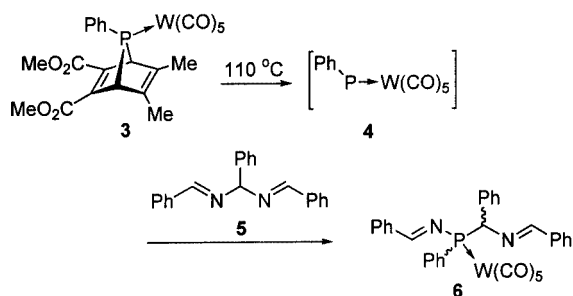
Compound **6** was obtained after column chromatography as a 4:1 diastereomeric mixture as determined by integration of its ^{31}P NMR resonances at δ = 81.8 and 81.2.[16] The major isomer was obtained after fractional crystallization. The presence of its two N=CH groups was evident from the ^{13}C NMR resonances at δ = 163.4 and 174.7 and the lowfield ^{1}H NMR resonances at δ = 7.99 and 8.72, the latter of which showed a typical $^3J_{P,H}$ coupling of 28.1 Hz. Its structure was established unequivocally by a single-crystal X-ray structure determination. The major isomer of **6** crystallized as two crystallographically independent molecules, of which one is depicted in Figure 1.[16b] This molecule has a P1−N1 bond 1.7148(19) Å long and two C=N bonds of 1.268(3) Å for both C1−N1 and N2−C3, which are conjugated with the phenyl rings as is evident from the relatively short C1−C4 and C3−C22 bonds of 1.471(3) Å and 1.475(3) Å, respectively. The phenyl rings are not coplanar with the C=N bonds, with torsion angles of 16.2(3), and 14.4(4)°.

The formation of **6** is exceptional. So far, insertion of RPW(CO)$_5$ into a C−N bond has been observed only for the reaction with a highly strained aziridine.[17] Insertions into C−H,[18] C−C,[19] and C−P[20] bonds are equally rare, whereas they are well established for acidic N−H or O−H bonds.[21] However, ab initio MO theory showed that singlet phosphinidene ^{1}PH should give an addition complex with NH$_3$ prior to N−H bond insertion.[22] Hence, formation of **6** by direct insertion of PhPW(CO)$_5$ into a C−N bond seemed unlikely.
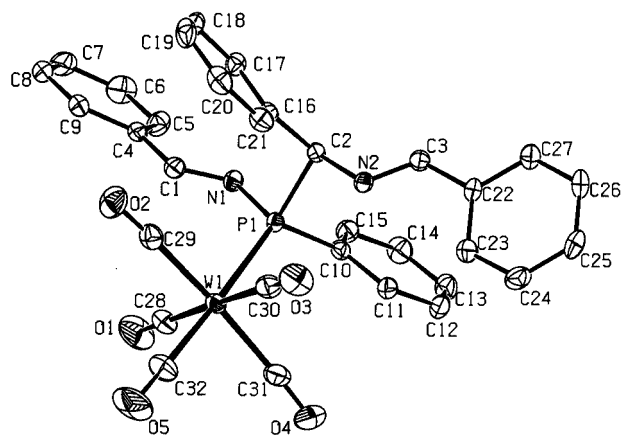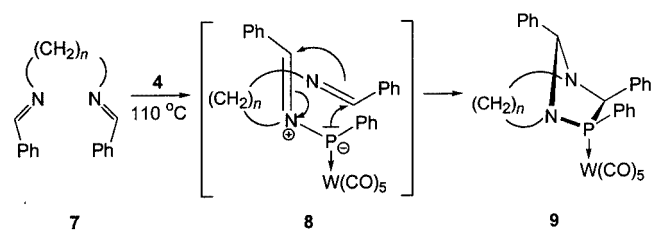

Figure 1. Displacement ellipsoid plot (50% probability level) of **6** in the crystal; only the major isomer was crystallized; the first of two crystallographically independent molecules is shown, with hydrogen atoms omitted for clarity; selected bond lengths [Å], angles and torsion angles [°]; the values for the second molecule are in square brackets: C1−N1 1.268(3) [1.265(3)], N1−P1 1.7148(19) [1.712(2)], P1−C2 1.889(2) [1.892(2)], C2−N2 1.460(3) [1.449(3)], N2−C3 1.268(3) [1.266(3)], P1−W1 2.5104(6) [2.5070(6)], P1−C10 1.819(2) [1.826(2)], C1−C4 1.471(3) [1.470(3)], C2−C16 1.507(3) [1.510(3)], C3−C22 1.475(3) [1.468(3)]; N1−C1−C4 122.9(2) [122.3(2)], C1−N1−P1 121.30(17) [122.89(17)], N1−P1−C2 99.81(9) [97.19(10)], P1−C2−N2 104.63(14) [107.56(15)], C2−N2−C3 117.43(19) [117.1(2)], N2−C3−C22 122.2(2) [123.3(2)], N1−P1−C10 99.18(10) [99.77(10)], N1−P1−W1 117.93(7) [119.46(7)]; P1−N1−C1−C4 179.15(16) [177.41(17)], C1−N1−P1−C2 −98.19(19) [−100.4(2)], N1−P1−C2−N2 −167.85(14) [−166.94(15)], P1−C2−N2−C3 129.65(18) [102.2(2)], C2−N2−C3−C22 −175.4(2) [179.4(2)], N1−C1−C4−C5 16.2(3) [−3.2(4)], N2−C3−C22−C23 14.4(4) [−11.3(4)]

What are the alternatives? Ylides can be subjected to 1,3-dipolar cycloadditions. For example, we showed recently that the transient P,N-ylide complexes **8**, in which the two imine groups are separated by two to four methylene units, undergo such a transformation to give **9** diastereoselectively.[7a] In the case of **10** this would result in a rather strained compound (**11**), which might ring-open to give product **6** [Equation (1)]. In fact, such a retro [2+2] cycloaddition of a 1,3-diazacyclobutane to yield two imines has been reported to proceed at temperatures below 35 °C.[23] Another possible route to **6** is a 2,3-sigmatropic shift of P,N-ylide **10** [Equation (2)], but these ylides are better known to give azaphosphiridines instead, which in this case would result in **12**, or to give extended structures by incorporation of another imine.[7,9]

(1)

(2)

12
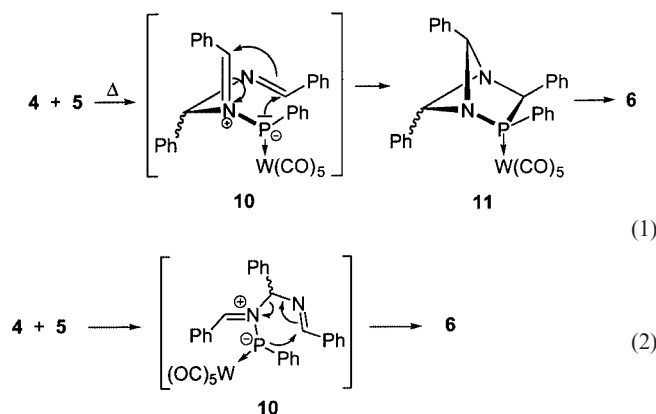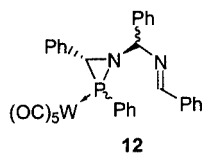
A priori, no differentiation between the two reaction pathways can be made. We therefore resorted to B3LYP/6-31G* calculations to explore the potential energy surface of a simplified parent system in which the W(CO)$_5$ group was absent and all the phenyl groups were replaced by hydrogen atoms.[24] Four minima were found in *anti* and *gauche* conformations: P,N-ylide **13**, bicyclic **14** (1 isomer), the formal insertion product **15**, and azaphosphiridine **16**. Their absolute and relative energies are listed in Table 1. The optimized geometries of the energetically preferred *gauche* conformers are shown in Figure 2.

Table 1. B3LYP/6-31G* absolute (in −a.u.) and relative (in kcal·mol^{-1}) energies for **13−19**

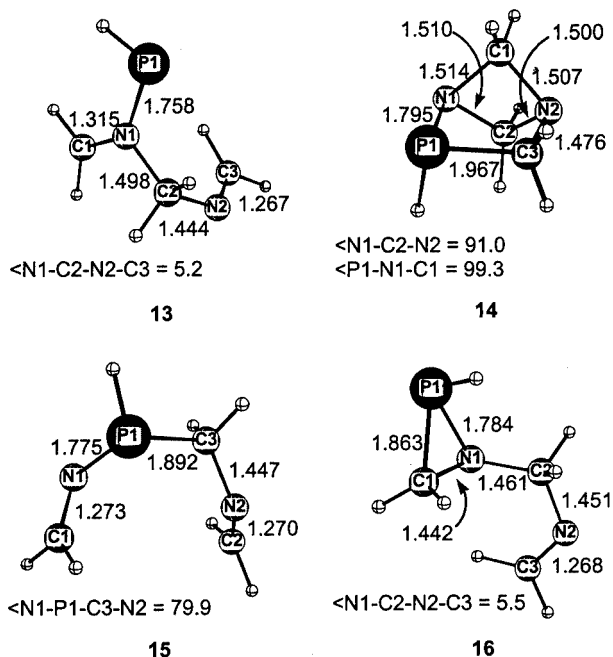| Compounds	E	ΔE
13, *gauche*	569.293458	0.0
13, *anti*	569.293220	0.2
14	569.297167	−2.3
15, *gauche*	569.321163	−17.4
15, *anti*	569.320448	−16.9
16, *gauche*	569.310107	−10.4
16, *anti*	569.307525	−8.8
17	569.241455	32.6
18, P−H *exo*	569.272740	13.0
18, P−H *endo*	569.270604	14.3
19, *gauche*	569.268119	15.9
19, *anti*	569.267762	16.1
20	569.243021	31.6

13

14

15

16

Figure 2. B3LYP/6-31G*-optimized geometries for structures **13−16**

The theoretical calculations indeed support the view that the first step in the reaction giving rise to the C−N insertion product is the presumed formation of P,N-ylide complex **10**. Namely, formation of **13** by the addition of singlet ^{1}PH to the nitrogen lone pair of one of the C=N groups of the parent bis(imine) is exothermic by 66.3 kcal·mol^{-1}. This ylide prefers the *gauche* conformation (N1−C2−N2−C3 = 5.2°) over the *anti* form (N1−C2−N2−C3 = 132.2°), albeit by only 0.2 kcal·mol^{-1}. Its ylide character is evident from the 1.315 Å C=N iminium bond, which is much longer than that of the imine group (1.267 Å).

Starting from this P,N-ylide **13**, the transition structures **17**, **18**, and **19** correspond to a 1,3-dipolar cycloaddition to bicyclic **14**, a 2,3-sigmatropic shift to C−N insertion product **15**, and ring-closure to azaphosphiridine **16**, respectively. A fourth transition structure (**20**) concerns the ring-opening of the four-membered ring of **14** to give product **15**. The nature of the transition structures was confirmed by intrinsic reaction coordinate calculations (IRC) that connected them with the associated minima. Their absolute and relative energies are given in Table 1. The geometries of the more stable *gauche* conformers are shown in Figure 3 and the energy profiles are depicted in Figure 4.

17

18

19

20
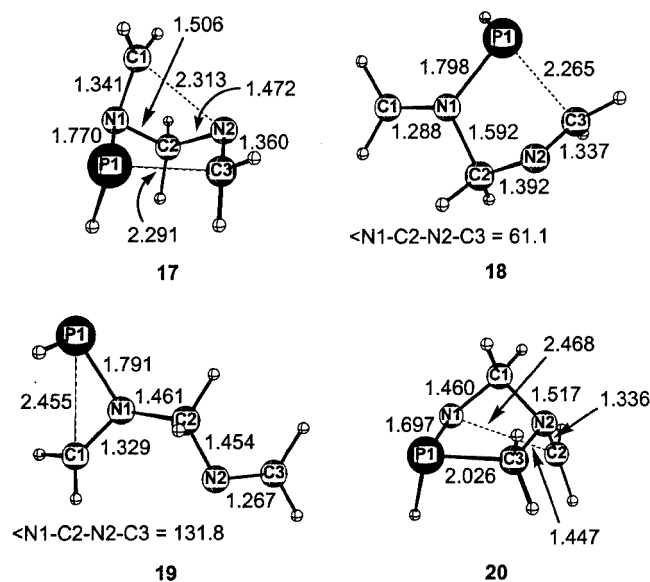
Figure 3. B3LYP/6-31G*-optimized geometries for transition structures **17−19**

Expectedly, C−N insertion structure **15** was the global minimum. The *gauche* conformation (N1−P1−C3−N2 = 79.9°) is favored over the *anti* form by 0.5 kcal·mol^{-1}. Its bond lengths are in good agreement with those experimentally ascertained for compound **6** in the crystal, except for the 0.06 Å longer N−P bond, which we attribute to the absence of the W(CO)$_5$ and phenyl groups in the calculated structure, and the presence of thermal motion in the experimental structure. The presence of these groups may also explain why the experimental structure prefers an *anti* conformation. Compound **15** is a substantial 17.4 kcal·mol^{-1} more stable than P,N-ylide **13**. 1,3-Dipolar cycloadduct **14**

Figure 4. B3LYP/6-31G* energy profile; carbon atoms are depicted in black, nitrogen atoms in white, and phosphorus atoms in gray

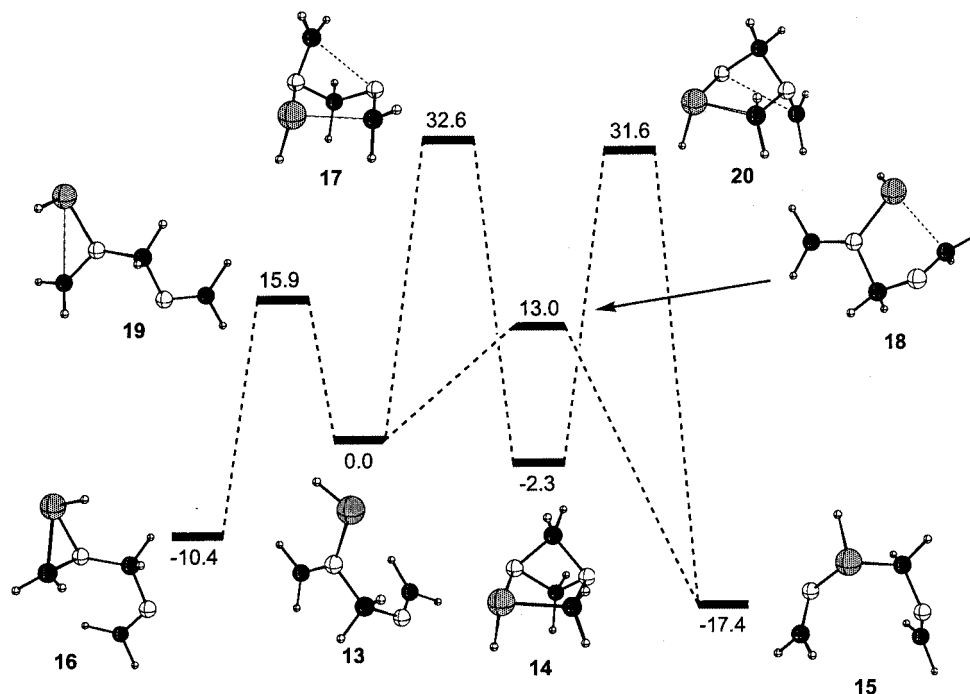and azaphosphiridine **16** are also favored over the ylide, but their respective energy differences of 2.3 and 10.4 kcal·mol^{-1} are much more modest.

Conversion of the ylide into the C−N insertion structure, representing a concerted 2,3-sigmatropic shift, requires only 13.0 kcal·mol^{-1}. The transition structure **18** for this process represents an early transition in which the negatively charged phosphorus atom of the P,N-ylide group attacks the more electropositive carbon atom of the nearby imine group. The P1−C3 interaction of 2.265 Å develops into a common bond, while the already elongated N1−C2 bond breaks. The envelope conformation of the five-membered ring of the transition structure resembles those reported for the 2,3-sigmatropic shifts of allylic sulfimines and sulfoximines,[25] and that of allylsulfonium methylide.[26] The *exo* conformer of **18**, with the P−H bond rotated away from N2, is favored over the *endo* form by only 1.3 kcal·mol^{-1}. This *exo/endo* preference determines the stereoselectivity of the reaction and should be influenced by the W(CO)$_5$ and Ph groups.

The energy profile for the parent system further suggests that the experimentally observed formation of **6** cannot occur via bicyclic **11**. Not only is the conversion of P,N-ylide **13** into **14** only modestly exothermic (0.5 kcal·mol^{-1}), but this 1,3-dipolar cycloaddition also has a substantial barrier (32.6 kcal·mol^{-1}), 19.6 kcal·mol^{-1} higher than that for the 2,3-sigmatropic shift. The origin of this far less favored pathway is attributable to the build-up of strain in bicyclic **14**, reflected, for example, in the small N1−C2−N2 and P1−N1−C1 angles of 91.0° and 99.3°, respectively. For comparison, the reported 1,3-dipolar cycloaddition of ylide **21** into the far less strained bicyclic **22** has a much higher exothermicity of 29.8 kcal·mol^{-1} and a much smaller en-

ergy barrier of only 10.7 kcal·mol^{-1}.[7a] The subsequent ring-opening to **15** has a surprisingly high (considering the strained nature of **14**) barrier of 31.6 kcal·mol^{-1}. IRC calculation from transition compound **20** revealed this process to proceed by consecutive scissions of the N1−C2 and N2−C1 bonds.
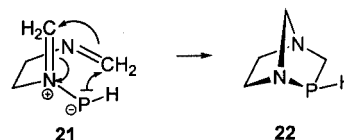
A simple ring-closure converts the P,N-ylide to azaphosphiridine **16**, which prefers a *gauche* conformation (N1−C2−N2−C3 = 5.5°), the *anti* form being 1.6 kcal/mol less stable. The P−C and P−N bond lengths in the three-membered ring compare well with a recently reported crystal structure for a W(CO)$_5$-complexed azaphosphiridine[9a] when the stabilizing effect of the W(CO)$_5$ group is taken into account.[27] However, neither the 10.4 kcal/mol exothermicity nor the activation energy of 15.9 kcal·mol^{-1} for formation of **16** make this process competitive with the 2,3-sigmatropic shift that directly affords **15**. It is not surprising then, that the W(CO)$_5$-complexed azaphosphiridine **12** is not observed in the reaction between **4** and **5**.

Conclusions

Experimental and theoretical evidence for the first 2,3-sigmatropic shift of a phosphane ylide is presented. This rearrangement of the W(CO)$_5$-complexed P,N-ylide, formed in situ, from a single-carbon-spaced bis(imine) to the C−N-

inserted product is both kinetically and thermodynamically favored over alternative reactions such as a 1,3-dipolar cycloaddition and ring-closure to a three-membered azaphosphiridine. Density functional theory at the B3LYP/6-31G* level for the parent system gave a remarkably small barrier of 13.0 kcal·mol^{-1} for the 17.4 kcal/mol exothermic 2,3-sigmatropic shift. Considering the general importance of 2,3-sigmatropic shifts,[13] this chemistry may now be expanded to enrich the synthetic applicability of transient electrophilic phosphinidene complexes.

Computational Section

All electronic structure calculations were carried out with the GAUSSIAN 98 suite of programs (G98). Becke's three-parameter hybrid exchange functional[28] combined with the Lee−Yang−Parr correlation functional,[29] denoted as B3LYP, and the 6-31G* basis set were used for the density functional theory (DFT) calculations. First- and second-order energy derivatives were computed to establish whether minima or transition structures had been located. Intrinsic reaction coordinate driving calculations (IRC) were performed to establish connections between transition structures and minima.

Experimental Section

General: The experiments were performed under dry nitrogen. Solids were dried in vacuo, and liquids were distilled (under N_2) prior to use. Solvents were used as purchased, except for toluene, which was distilled from sodium, and Et_2O, which was distilled from $LiAlH_4$. NMR spectra were recorded with Bruker AC 200 (^1H, ^{13}C) and WM 250 spectrometers (^{31}P) with $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. High-resolution mass spectra (HR-MS) were recorded with a Jeol JMS SX/SX102A by the Institute for Mass Spectrometry at the University of Amsterdam. Complex **3**[30] and bis(imine) **5**[31] were prepared according to literature procedures.

Pentacarbonyl(1,3,4,6-tetraphenyl-2,5-diaza-3-phospha-1,5-hexadiene-κP)tungsten (6): A solution of complex **3** (0.40 g, 0.61 mmol) and **5** (0.18 g, 0.61 mmol) in toluene (3.5 mL) was stirred at 110 °C for 10.5 h. Evaporation of the solvent and purification of the residue by chromatography on silica gel 60 (0.2−0.5 mm) with Et_2O/ pentane (1:20) gave 0.22 g (58%) of **6** as a mixture of diastereomers in a 4:1 ratio and as a yellow solid. Crystallization from Et_2O/ pentane afforded the major diastereomer as yellow crystals. *Major isomer:* m.p. 159−160 °C. ^{31}P NMR (toluene): δ = 81.2 ($^1J_{W,P}$ = 258.5 Hz). ^1H NMR (CDCl$_3$): δ = 4.96 (d, $^2J_{P,H}$ = 1.4 Hz, 1 H, PCH), 7.05−7.86 (m, 20 H, Ph), 7.99 (d, $^4J_{P,H}$ = 3.1 Hz, 1 H, PCN=CH), 8.72 (d, $^3J_{P,H}$ = 28.1 Hz, 1 H, PN=CH). ^{13}C NMR (CDCl$_3$): δ = 82.4 (d, $^1J_{P,C}$ = 31.4 Hz, PC), 129.2−133.1 (m, Ph), 135.9 (d, $^1J_{P,C}$ = 28.9 Hz, P-ipso-Ph), 136.1 (s, CN=C-ipso-Ph), 136.2 (s, PN=C-ipso-Ph), 137.4 (d, $^2J_{P,C}$ = 1.8 Hz, PC-ipso-Ph), 163.4 (d, $^3J_{P,C}$ = 12.2 Hz, PCN=C), 174.7 (s, PN=C), 196.4 (dd, $^2J_{P,C}$ = 7.2, $^1J_{W,C}$ = 125.4 Hz, CO *cis*), 198.6 (d, $^2J_{P,C}$ = 25.8 Hz, CO *trans*). HR-MS: calcd. for $C_{32}H_{24}N_2O_5PW$ [M + H] 731.0938, found 731.0874 (δ = 2.0·10^{-2}); *minor isomer* (in the mixture): ^{31}P NMR (toluene): δ = 81.8. ^1H NMR (CDCl$_3$): δ = 4.97 (d, $^2J_{P,H}$ = 5.3 Hz, 1 H, PCH), 7.0−7.9 (m, 20 H, Ph), 8.07 (d, $^4J_{P,H}$ = 3.0 Hz, 1 H, PCN=CH), 8.69 (d, $^3J_{P,H}$ = 27.2 Hz, 1 H, PN=CH). ^{13}C NMR (CDCl$_3$): δ = 82.5 (d, $^1J_{P,C}$ = 33.0 Hz, PC), 127.6−136.9 (m, Ph), 164.0 (d, $^3J_{P,C}$ = 13.1 Hz, PCN=C), 174.2 (s, PN=C), 196.4 (dd, $^2J_{P,C}$ = 7.1, $^1J_{W,C}$ = 125.4 Hz, CO *cis*), 198.5 (d, $^2J_{P,C}$ = 26.2 Hz, CO *trans*).

Crystal Structure Determination of 6: $C_{32}H_{23}N_2O_5PW$ (730.34), yellowish block, 0.48 × 0.24 × 0.24 mm, monoclinic, $P2_1/c$ (no. 14), a = 20.4825(1), b = 12.4624(1), c = 27.7591(2) Å, β = 123.1141(4)°, V = 5934.97(7) Å^3, Z = 8, ρ = 1.635 g·cm^{-3}, 98741 measured reflections, 13566 unique reflections (R_{int} = 0.067). Intensities were measured with a Nonius KappaCCD diffractometer with rotating anode (Mo-K_α, λ = 0.71073 Å) at a temperature of 150 K. Analytical absorption correction by use of the program PLATON[32] (routine ABST, μ = 3.99 mm^{-1}, 0.33−0.46 transmission). The structure was solved with automated Patterson methods with the program DIRDIF97[33] and refined with the program SHELXL97[34] against F^2 of all reflections up to a resolution of (sin θ/λ)$_{max}$ = 0.65 Å^{-1}. The asymmetric unit contains two independent molecules, which mainly differ in the conformations of the phenyl groups at C4 and C22. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. R [$I > 2σ(I)$]: $R1$ = 0.0219, $wR2$ = 0.0505. R (all data): $R1$ = 0.0299, $wR2$ = 0.0533. S = 1.024. Residual electron density between −0.93 and 0.92 e/Å^3. The drawings, structure calculations, and checking for higher symmetry was performed with the program PLATON.[29] CCDC-167160 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[15] While bis(imine) **5** is readily available,[31] we are unaware of synthetic routes to bis(imines) separated by an unsubstituted methylene bridge.

[16] [16a] The ³¹P NMR spectrum of the crude reaction mixture showed one other resonance from an unidentified product in this region at δ = 74.4 (ca. 5−7%). [16b] Each of the two diastereoisomers of **6** can have (*E*) and (*Z*) configurations for each of its imine groups, but in the light of the limited configurational stability of imines in general we assume that the minor isomer of **6**, like the major product (vide infra), also has an (*E*) configuration for both of them.

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