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Azaphospiridine Complexes

Stimuli-Responsive Frustrated Lewis-Pair-Type Reactivity of a Tungsten Iminoazaphosphiridine Complex

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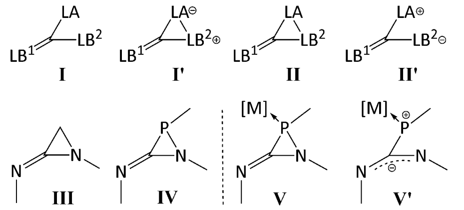
Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: Reactions of 3-imino-azaphosphiridine complexes **1a,b** with carbodiimides **2a,b**, isocyanates **3a,b**, and carbon dioxide are described. Whereas exchange of the carbodiimide unit occurs in the first case, an overall ring expansion takes place with phenyl isocyanate (**3a**) and carbon dioxide to yield complexes **4** and **5** bearing novel 1,3,5-oxazaphospholane ligands; the isopropyl derivative **3b** did not react under these conditions. DFT calculations provide insight into the pathway of the reaction with carbon dioxide with model complex **1c**, revealing effects of initial non-covalent interactions with the substrate onto the ring bonding, thus triggering an initially masked frustrated Lewis-pair-type behavior.

Recently, the challenge was solved of building up an array of three atoms in a molecular compound, two of which have no bonding interactions and being opponents in terms of the Lewis acid–base concept; this has been termed a frustrated Lewis pair (FLP).[1] Due to this, a wide range of new chemical structures such as **I** were discovered in recent years[2] (**I,I′**: $LB^1=CR_2$; Scheme 1); evidence for **I′** was not obtained so far. Among the many interesting transformations enabled by **I** is the activation of quite unreactive substrates such as H_2 and CO_2 through interactions of LA/LB centers such as B/P[3] and Al/P.[4]



Scheme 1. 1,1′-Vinyl-derived frustrated Lewis pairs **I**, closed isomers **I′**, and neutral rings with polar bonds **II** and zwitterions thereof **II′** ($LB^1=CR_2$); 3-imino-aziridines **III**, 3-imino-azaphosphiridines **IV** and their complexes **V**, **V′**. Lines denote organic substituents, [M] a transition-metal complex, LA = Lewis acid, and LB = Lewis base.

To approach the FLP concept from a different angle, we contemplated the necessities to enhance reactivity of three-membered heterocycles having three different, strongly polarized ring bonds,[5] high ring strain being combined with an *exo* nucleophilic center LB^1.[6] Since it is well known that implementation of an sp^2-hybridized center increases ring strain in three-membered P-heterocycles[7] and bond strain in the distal bond, we started to study heterocycles of type **II** possessing a phosphorus unit in reactions with important heterocumulenes, that is, RN=C=NR, RN=C=O, CO_2. Until recently, only 3-iminoaziridines **III**[8] were at hand, and **IV** remained unknown. On the other hand, it has been recently shown that dinuclear phosphinidene complexes react with carbodiimides to form a wealth of interesting N,P,C-heterocycles,[9] but complexes of type **V** have not been obtained by this route. Complexes **V**, which have been described recently,[10] appear as particularly interesting targets as they may feature a masked (crypto) FLP-type character that is ready to be unveiled upon cleavage of a markedly weakened endocyclic P–N bond (**V′**).

Herein, an unusual exchange reaction of 3-iminoazaphosphiridine complexes is described in the case of carbodiimides, whereas isocyanates and carbon dioxide lead to an overall ring expansion, thus yielding novel five-membered N,P,C-heterocyclic ligands. DFT calculations provide insight into the latter pathway.

When the 3-iminoazaphosphiridine complex **1a**[10] was allowed to react with 1 equiv of dicyclohexyl carbodiimide (**2b**) in THF at ambient temperature, a mixture of **1a** and **1b** (ratio 1:1) was obtained after 3 h (Scheme 2); this ratio remained constant over time. Apparently, an unusual substitution reaction had occurred in which the diisopropyl carbodiimide moiety in **1a** was exchanged[11] by the dicyclohexyl carbodiimide to form **1b**. Besides the evidence obtained from the

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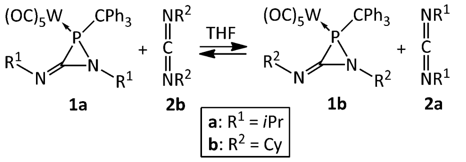
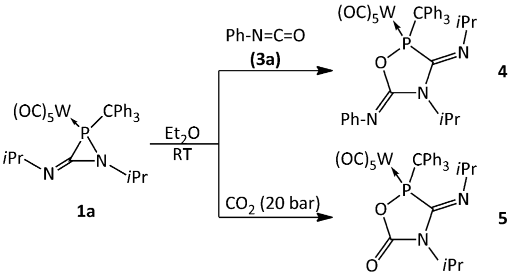


Scheme 2. Carbodiimide exchange reaction of 3-iminoazaphosphiridine complex **1a**.

^{31}P{^{1}H} NMR spectra, the nature of the newly formed product as **1b** was further confirmed through formation of a 1:1 mixture of their hydrolysis products upon reaction of **1a,b** with water.[10,12] To examine this exchange further, the alternative reaction of **1b** with carbodiimide **2a** was performed, and again a 1:1 mixture was formed.

When 3-iminoazaphosphiridine complex **1a** was treated with 1 equiv of phenyl isocyanate (**3a**) in Et_2O or THF at ambient temperature (Scheme 3), 1,3,5-oxazaphospholane complex **4** was obtained; interestingly, no reaction was observed when isopropyl isocyanate (**3b**) was used under the same conditions. Complex **4** showed a ^{31}P{^{1}H} resonance at 131.7 ppm ($^{1}J_{W,P} = 277.7$ Hz); this was accompanied by the formation of a complex (ca. 4%; ^{31}P{^{1}H} = 103.4 ppm, $^{1}J_{W,P} = 288.0$ Hz) that could not be identified. The ^{13}C{^{1}H} NMR spectra of **4** revealed resonances for the imino carbon atoms at 143.5 ppm ($^{2+3}J_{P,C} = 12.4$ Hz) and 150.7 ppm ($^{1+4}J_{P,C} = 10.2$ Hz). In the case of **4**, a formal insertion of the carbonyl group of the phenyl isocyanate into the P–N bond of complex **1a** had occurred, whereby **4** was isolated in 65% yield and its molecular structure was confirmed by X-ray analysis (Figure 1).



Scheme 3. Reactions of 3-iminoazaphosphiridine complex **1a** with phenyl isocyanate (**3a**) and CO_2 to give complexes **4** and **5**.

To test its reactivity, **1a** was reacted with carbon dioxide first in THF (1 bar, RT) to give readily 1,3,5-oxazaphospholane complex **5** via ring expansion (Scheme 3). Under these conditions about 15% of an unknown complex was observed (δ ^{31}P{^{1}H} = 71.6, $^{1}J_{W,P} = 288.0$ Hz, $^{1}J_{P,H} = 358.5$ Hz) that could not be isolated. This by-product formation was suppressed if the reaction was carried out in Et_2O at 20 bar and ambient temperature. Product **5** (δ ^{31}P{^{1}H} = 128.0, $^{1}J_{W,P} = 272.4$ Hz) was fully characterized including X-ray structure analysis (Figure 2) and showed ^{13}C{^{1}H} NMR resonances of 151.0 ppm ($^{1+4}J_{P,C} = 8.1$ Hz) and 149.5 ($^{2+3}J_{P,C} = 12.1$ Hz) for the imino and carbonylic carbon atoms, respectively. The 1,3,5-oxazaphospholane rings in **4** and **5** are planar, and the sum of bond angles at both N1 atoms (**4**: 359.9°; **5**: 360.0°) shows a planar environment.

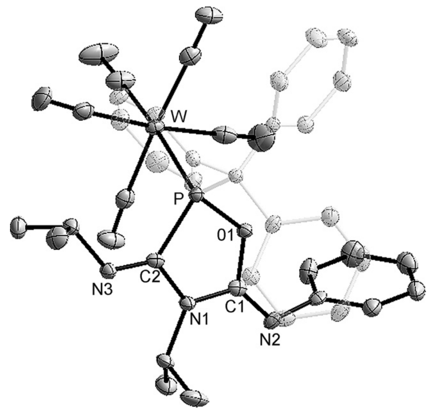


Figure 1. Molecular structure of 1,3,5-oxazaphospholane complex **4** (ellipsoids set at 50% probability, hydrogen atoms are omitted and CPh_3 group shown in gray for clarity). Selected structural parameters (distances [Å] and angles [°]): P–W 2.5011(6), P–C2 1.885(2), P–O1 1.6562(15), O1–C1 1.386(2) C1–N1 1.370(3), N1–C2 1.406(3); C2-P-O1 89.98(9), O1-C1-N1 111.20(19), N1-C2-P 105.21(15).

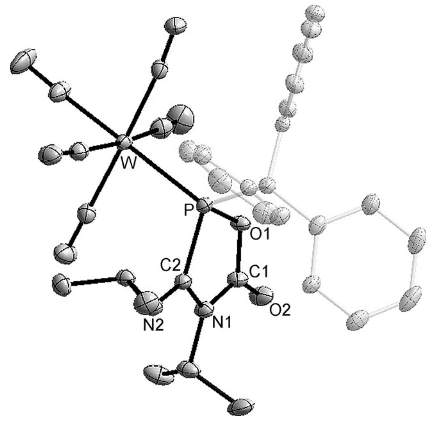
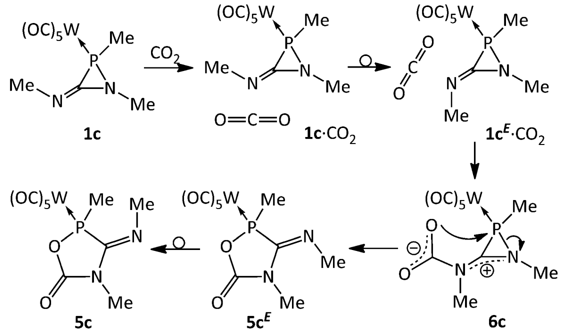


Figure 2. Molecular structure of 1,3,5-oxazaphospholane complex **5** (ellipsoids set at 50% probability, hydrogen atoms are omitted for clarity). Selected structural parameters (distances [Å] and angles [°]): P–W 2.4935(8), P–C2 1.885(3), P–O1 1.671(3), O1–C1 1.377(4), C1–N1 1.370(5), N1–C2 1.407(4); C2-P-O1 89.82(14), O1-C1-N1 111.2(3), N1-C2-P 104.9(2).

To understand the formal P–N bond-selective ring expansion process, quantum chemical calculations ($COSMO_{toluene}$/DLPNO-CCSD(T)/def2-TZVPPecp//$COSMO_{toluene}$/B3LYP-D3/def2-TZVP ecp)[13] were performed to elucidate the reaction pathway. Here, the calculated reaction with carbon dioxide (for details of the computations, see the Experimental Section and the Supporting Information) of model complex **1c** was explored (methyl groups at both P and N atoms were used for the sake of computational efficiency). Initially, the basic exocyclic N atom of the most stable *Z*-configured initial model complex **1c**[10] interacts with the electrophilic center of carbon dioxide leading to **1c**·CO_2 that undergoes rotation of the weakened exocyclic C–N bond to afford the van der Waals complex



Scheme 4. Proposed mechanism for the formation of **5 c**.

1 c^E·CO_2 bound by weak non-covalent interactions (NCIs; Scheme 4).

The van der Waals complex **1 c**^{E}·CO_2 is easily visualized by the NCIplot technique of color-coded reduced density gradient (RDG) isosurfaces (Figure 3).[17] The most significant NCIs are those linking the exocyclic N atom with the CO_2 carbon ($d=$ 2.858 Å; WBI$=$0.010; $\rho(r)=1.15\times10^{-2}$ e/a_o^3) and one CO_2 oxygen atom with the P atom ($d=3.330$ Å; WBI$=$0.003; $\rho(r)=0.68\times10^{-2}$ e/a_o^3) and a carbonyl ligand ($d=3.205$ Å; WBI$=$0.002; $\rho(r)=0.51\times10^{-2}$ e/a_o^3).

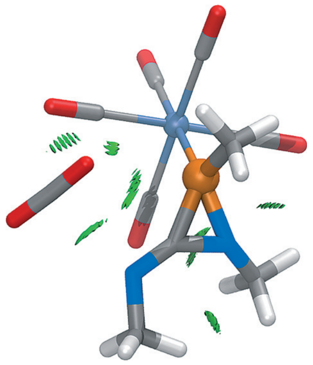


Figure 3. Computed (B3LYP-D3/def2-TZVPecp) most stable structure for van der Waals complex **1**^{E}**c**·CO_2 with NCIplot highlighting key stabilizing NCIs. The RDG $s=0.28$ au isosurface is colored over the range $-0.05<\mathrm{sign}(\lambda_2)\cdot\rho<0.05$ au: blue denotes strong attraction, green stands for moderate interaction, and red indicates strong repulsion.

Strengthening of the N⋯C interaction in the van der Waals complex leads to zwitterionic intermediate **6 c** that undergoes ring opening by attack of the negatively charged O atom to phosphorus thus forming a new five-membered 1,3,5-oxazaphospholane ring **5 c**^{E} in a highly exergonic low-barrier process (Figure 4). Finally the exocyclic *E*-configured C=N bond rotates to give the most stable *Z*-configuration of the final product **5 c**.

The driving force for the overall transformation **1 c**$+CO_2\rightarrow$ **5 c** must be mainly related to the release of the remarkably high ring strain (50.58 kcal mol^{-1} was reported for the parent complex).[10,18] In line with this, the computationally inexpensive $G(r)$ (Lagrangian of the kinetic energy density at ring critical points)[19] values reveal a dramatic increase of ring strain on moving from **1 c** to **1 c**^{E}·CO_2 and to **6 c** (Table 1), which parallels a weakening of the P–N bond. This situation approaches a bonding described by formula **II**′ (or more specifically **V**′) as result of an external substrate stimulus. Some commonly used bond-strength-related parameters support this view (Table 1).

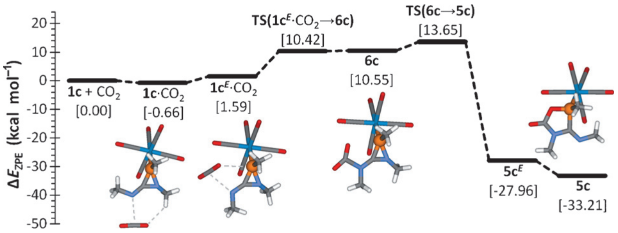


Figure 4. Computed ($COSMO_{toluene}$/DLPNO-CCSD(T)/def2-TZVPPecp) minimum energy path for the transformation **1 c**$+CO_2\rightarrow$**5 c**.

Table 1. Ring strain and parameters related to P–N bond strength for selected computed species.

Entry	$G(r)_{RCP}$[a]	d_{P-N}[b]	WBI_{P-N}	$\rho(r)_{P-N}$[c]
1 c	0.1362	1.747	0.748	0.1507
1 c^E·CO_2	0.1483	1.750	0.739	0.1493
6 c	0.1621	1.768	0.673	0.1389

[a] In au. [b] In Å. [c] In e/a_o^3.

In conclusion, evidence was presented that the 3-iminoazaphosphiridine ring in **1** allows for an unusual carbodiimide exchange, but also displays a masked FLP-type reactivity which comes to the fore upon interaction with a substrate, as illustrated by the reactions with phenyl isocyanate and carbon dioxide. Interestingly, use of isopropyl isocyanate led to no reaction, that is, substrate discrimination. Quantum chemical calculations unveiled that the initial non-covalent interaction of the *exo* nitrogen center with the substrate enhances ring strain and hence triggers cleavage of the weakened distal P–N bond, thus increasing the electrophilicity of the P center and provoking its reaction with the O atom of the carbonyl unit.

Experimental Section

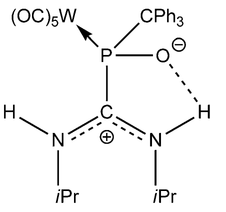
Preparative methods

All reactions and manipulations were carried out under an atmosphere of dry argon, using Schlenk and vacuum-line techniques or glove-box. Argon was cleaned over a BTS catalyst; Ar gas was dried using silica gel and P_2O_5. Solvents were dried according to standard procedures using sodium or sodium/benzophenone and stored under inert gas atmosphere.

General procedure for the synthesis of 1 a,b: *tert*-Butyllithium (1.6 M in *n*-hexane, 1.1 equiv) was slowly added to a THF solution of triphenylmethyl dichlorophosphane tungsten(0) complex and 12-crown-4 (1 equiv) at −78 °C. After 15 min, *N,N*′-dialkyl carbodiimide **2 a,b** (1 equiv) was slowly added at −78 °C. The reaction solution was stirred and warmed up slowly to +4 °C and then kept at 4 °C for 15 h. Afterwards, the solvent was removed in vacuo (ca. 10^{-2} mbar) and LiCl filtered from an *n*-pentane solution.

1a: Yellow solid, yield: 900 mg (1.24 mmol, 87%), m.p. 120–121 °C, ^{1}H NMR ($CDCl_3$): $\delta=0.80$ (d, 3H, P-*N*-CH-C*H*$_3$, $^{3}J_{H,H}=6.5$ Hz), 0.80 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=6.2$ Hz), 1.17 (d, 3H, P-*N*-CH-C*H*$_3$, $^{3}J_{H,H}=6.5$ Hz), 1.29 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=6.3$ Hz), 3.35 (dsept, 1H, N-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=6.5$ Hz, $^{3}J_{P,H}=3.8$ Hz), 3.44 ppm (sept, 1H, N-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=6.3$ Hz); ^{13}C NMR ($CDCl_3$): $\delta=19.6$ (d, P-*N*-CH-*C*H$_3$, $^{3}J_{P,C}=2.7$ Hz), 20.3 (d, P-*N*-C-CH$_3$, $^{3}J_{P,C}=1.7$ Hz), 23.1 (s, C=N-C-CH$_3$), 24.1(s, C=N-C-CH$_3$), 50.6 (s, P-*N*-CH-CH$_3$), 56.9 (d, N-CH-CH$_3$, $^{3}J_{P,C}=14.3$ Hz), 65.6 (d, P-*C*-Ph$_3$, $^{1}J_{P,C}=15.8$ Hz), 125.1 (s, Ph), 127.2 (s, Ph), 128.5 (s, Ph) 130.0 (d, ^{ipso}Ph, $^{2}J_{P,C}=9.8$ Hz), 137.0 (d, N=*C*, $^{1}J_{P,C}=7.2$ Hz), 140.4 (d, Ph, $J_{P,C}=3.0$ Hz), 143.0 (s, Ph), 194.6 (dSat, $^{2}J_{P,C}=6.5$ Hz, $^{1}J_{W,C}=126.3$ Hz, *cis*-CO), 196.1 ppm (d, $^{2}J_{P,C}=35.9$ Hz, *trans*-CO); ^{31}P NMR ($CDCl_3$): $\delta=2.1$ ppm, $^{1}J_{W,P}=257.4$ Hz; MS (EI, 184W): *m/z* (%): 724.1, $[M]^+$, (0.3); 598.0, $[M]^+-i$PrN=C=N*i*Pr (0.3); 570.0, $[M]^+-i$PrN=C=N*i*Pr −CO, (0.03); 542.0, $[M]^+$-*i*PrN=C=N*i*Pr −2xCO, (0.1); 514.0,$[M]^+-i$PrN=C=N*i*Pr 3×CO, (0.5); 483.0, $[M]^+-i$PrN=C=N*i*Pr −4×CO,(0.03); 458.0, $[M]^+-i$PrN=C=N*i*Pr −5×CO (1.2), 243.1, $[CPh_3]^+$ (70), 69.1, $[M]^+-i$PrN=C (100); IR (ATR): $\tilde{\nu}=2969$ (b, ν-CH$_2$), 2072 (s, ν-CO), 1980 (s, ν-CO), 1917 (s, ν-CO), 1740 (s, ν-CO), 1597 cm^{-1} (b, ν-C=N); elemental analysis (%) calcd for $C_{31}H_{29}N_2O_5PW$: C 51.40, H 4.04, N 3.87; found: C 53.21, H 4.63, N 3.59.

General procedure for the synthesis of hydrolysis products of 1a,b: Water (1 equiv) was added to a THF solution of **1a,b** at room temperature. The reaction mixture was stirred for 5 min. The solvent was removed in vacuo (ca. 10^{-2} mbar) and a yellow oil was obtained. The compound was then crystallized from pure Et_2O at −20 °C.



Hydrolysis product of 1a: White solid, yield = 250 mg (0.34 mmol, 70%), m.p. 162–163 °C, ^{1}H NMR ($CDCl_3$): $\delta=1.0$–1.4 (m, 12H, ^{iPr}C*H*$_3$), 3.9 (bs, 2H, ^{iPr}C*H*), 6.7–7.7 ppm (m, 3×Ph), N-*H* are in coalescence process at room temperature; ^{13}C NMR ($CDCl_3$): $\delta=22.8$ (s, *i*Pr-CH$_3$), 22.9 (s, *i*Pr-CH$_3$), 47.0 (s, 2 x ^{iPr}CH), 69.0 (d, $^{1}J_{C,P}=2.6$ Hz, P-CPh$_3$), 126.0 (d, $J_{C,P}=1.0$ Hz, *C*-Ph), 127.0 (d, $J_{C,P}=1.7$ Hz, *C*-Ph), 127.1 (d, $J_{C,P}=1.0$ Hz, *C*-Ph), 127.4 (d, $J_{C,P}=2.3$ Hz, *C*-Ph), 128.0 (s, *C*-Ph), 128.5 (s, *C*-Ph), 130.0 (d, $J_{C,P}=6.4$ Hz, *C*-Ph), 130.5 (d, $J_{C,P}=2.3$ Hz, *C*-Ph), 131.1 (d, $J_{C,P}=7.4$ Hz, *C*-Ph), 140.3 (d, $^{2}J_{C,P}=5.13$ Hz, *C*^{ipso}-Ph), 141.4 (d, $^{2}J_{C,P}=2.3$ Hz, *C*^{ipso}-Ph), 144.7 (d, $^{2}J_{C,P}=10.7$ Hz, *C*^{ipso}-Ph), 172.5 (d, N-C-N, $^{1}J_{P,C}=32.5$ Hz), 197.7 (dSat, $^{2}J_{P,C}=8.4$ Hz, $^{1}J_{W,C}=127.5$, *cis*-CO), 200.4 ppm (d, $^{2}J_{P,C}=27.5$ Hz, *trans*-CO, $^{1}J_{W,C}=144.2$, *trans*-CO); ^{31}P NMR ($CDCl_3$): $\delta=92.4$ ppm, qSat, $^{1}J_{W,P}=285.6$ Hz, $J_{P,H}=16.$ Hz; MS (EI, 184W): *m/z* (%): 743.1, $[M]^+$, (1); 658.1, $[M]^+-3$×CO, (2); 630, $[M]^+-4$×CO,(1); 243.1, $[CPh_3]^+$ (100); IR (ATR): $\tilde{\nu}=3347$ (b, N-H), 2967 (b, ν-CH$_2$), 2068 (s, ν-CO), 1986 (s, ν-CO), 1933 (s, ν-CO), 1915 (s, ν-CO), 1899 (s, ν-CO), 1607 cm^{-1} (b, ν-C=N); elemental analysis calcd (%) for $C_{31}H_{31}N_2O_6PW$: C 50.15, H 4.21, N 3.77; found: C 49.99, H 4.37, N 3.79.

4: Phenyl isocyanate **3a** (82.2 mg, 1 equiv) was added to a solution of iminoazaphosphiridine complex **1a** (500 mg, 0.69 mmol) in Et_2O at room temperature and stirred for 5 h. The solvent was removed in vacuo (ca. 10^{-2} mbar) and a dark yellow oil was obtained. The product was then crystallized from Et_2O at −20 °C and obtained as white solid; yield: 380 mg (0.45 mmol, 65%), m.p. 148–149 °C; ^{1}H NMR ($CDCl_3$): $\delta=0.46$ (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=5.9$ Hz), 1.12 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=5.8$ Hz), 1.46 (d, 3H, C-N-CH-C*H*$_3$, $^{3}J_{H,H}=6.9$ Hz), 1.56 (d, 3H, C-*N*-CH-C*H*$_3$, $^{3}J_{H,H}=7.0$ Hz), 3.48 (sept, 1H, C=N-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=5.8$ Hz), 4.89 (sept, 1H, C-*N*-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=6.9$ Hz), 6.5–7.7 ppm (m, 15H, 3×C$_6$*H*$_5$); ^{13}C NMR ($CDCl_3$): $\delta=17.5$ (s, C-*N*-CH-CH$_3$), 18.5 (s, C-*N*-CH-CH$_3$), 23.4 (s, C=N-CH-CH$_3$), 24.7 (s, C=N-CH-CH$_3$) 48.7 (s, C-*N*-CH), 56.2 (d, $^{3}J_{P,C}=12.5$ Hz C=N-*C*H), 71.2 (d, *C*Ph$_3$, $^{1}J_{P,C}=4.1$ Hz), 122.8 (s, C-*C*^{Ph}), 122.9 (s, C-*C*^{Ph}), 128.0 (s, C-*C*^{Ph}), 128.1(d, $J_{P,C}=1.7$ Hz C-*C*^{Ph}), 128.4(d, $J_{P,C}=1.5$ Hz C-*C*^{Ph}), 128.4 (s, C-*C*^{Ph}), 128.7 (s, C-*C*^{Ph}), 130.9 (d, $J_{P,C}=2.3$ Hz C-*C*^{Ph}), 131.2 (d, $J_{P,C}=8.6$ Hz C-*C*^{Ph}), 131.7 (d, $J_{P,C}=6.3$ Hz C-*C*^{Ph}), 137.6 (d, $^{2}J_{P,C}=6.5$ Hz C-*C*$^{ipso-Ph}$), 138.9 (d, $^{2}J_{P,C}=6.7$ Hz C-*C*$^{ipso-Ph}$), 141.9 (d, $^{2}J_{P,C}=8.1$ Hz C-*C*$^{ipso-Ph}$), 143.5 (d, $^{2}J_{P,C}=12.4$ Hz, *C*=N-Ph), 145.6 (s, N-*C*$^{ipso-Ph}$), 150.7 (d, $^{1}J_{P,C}=10.2$ Hz, *i*Pr-N=*C*), 195.2 (dSat, $^{2}J_{P,C}=6.2$ Hz, $^{1}J_{W,C}=127.1$, *cis*-CO), 197.5 ppm (d, $^{2}J_{P,C}=34.1$ Hz, *trans*-CO); ^{31}P NMR ($CDCl_3$): $\delta=125.06$ ppm, $^{1}J_{W,P}=273.8$ Hz. MS (EI, 184W) : *m/z* (%):843.1, $[M]^+$, (0.12); 787.2, $[M]^+-2$×CO (0.1); 759.2, $[M]^+-3$×CO, (0.1); 559.0, $[M]^+-CPh_3-3$×CO, (0.1); 488.9, $[M]^+-CPh_3-3$×CO, (0.12); 243.1 $[CPh_3]^+$; IR (ATR): $\tilde{\nu}=2971$ (b, ν-CH$_2$), 2928 (b, ν-CH$_2$), 2077 (s, ν-CO), 1997 (s, ν-CO), 1933 (s, ν-CO), 1697 (s, ν-CO), 1630 (b, ν-C=N), 1594 cm^{-1} (b, ν-C=N); elemental analysis calcd (%) for $C_{38}H_{34}N_3O_6PW$: C 54.11, H 4.06, N 4.98; found: C 53.97, H 4.11, N 4.98.

5: Route a: A solution of **1a** was freshly prepared: *tert*-butyllithium (1.6 M in *n*-hexane, 0.30 mL, 1.1 equiv) was slowly added at −78 °C to triphenylmethyl(dichloro)phosphane tungsten complex (295 mg, 0.44 mmol) and 12-crown-4 (69.4 μL, 1 equiv). *N,N'*-Diisopropyl carbodiimide **2a** (69.5 mL, 1 equiv) was then slowly added at −78 °C for 15 min. The reaction solution was stirred and warmed up slowly to +4 °C and then kept at 4 °C for 15 h. Afterwards, CO_2 was bubbled through the solution during 30 min and then LiCl was filtered off (Al_2O_3) from a 1:1 mixture of petroleum ether (40:60) and Et_2O at 25 °C, and the main impurity was extracted with *n*-pentane at room temperature. The product was then crystallized from Et_2O at −20 °C and obtained as light yellow solid; yield: 100 mg (0.14 mmol, 30%).

Route b: A solution of 3-imino-azaphosphiridine complex **1a** (100 mg, 0.14 mmol) in Et_2O (5 mL) was stirred under a CO_2 atmosphere (20 bar) for 15 h. The solvent was removed in vacuo (ca. 10^{-2} mbar) and a yellow oil was obtained. The product was then crystallized from Et_2O at −20 °C and obtained as a white solid; yield: 75 mg (0.98 mmol, 70%); m.p. 155–156 °C, ^{1}H NMR (C_6D_6): $\delta=0.27$ (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=5.8$ Hz), 0.94 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}=5.8$ Hz), 1.04 (d, 3H, C-*N*-CH-C*H*$_3$, $^{3}J_{H,H}=7.0$ Hz), 1.11 (d, 3H, C-*N*-CH-C*H*$_3$, $^{3}J_{H,H}=7.0$ Hz), 3.48 (sept, 1H, C=N-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=5.8$ Hz), 4.52 (sept, 1H, C-*N*-C*H*(CH$_3$)$_2$, $^{3}J_{H,H}=7.0$ Hz), 6.8–7.8 ppm (m, 15H, 3×C$_6$*H*$_5$); ^{13}C NMR (C_6D_6): $\delta=18.2$ (s, C-*N*-CH-CH$_3$), 18.5 (s, C-*N*-CH-CH$_3$), 23.4 (s, C=N-CH-CH$_3$), 24.8 (s, C=N-CH-CH$_3$), 48.0 (s, C-*N*-CH), 55.6 (d, $^{1}J_{P,C}=11.7$ Hz, C=N-*C*H), 71.2 (d, *C*Ph$_3$, $^{1}J_{P,C}=2.2$ Hz), 128.5 (d, $J_{P,C}=2.0$ Hz C-*C*^{Ph}), 128.6 (d, $J_{P,C}=2.7$, Hz C-*C*^{Ph}), 128.9 (s, C-*C*^{Ph}), 129.2 (s, C-*C*^{Ph}), 129.8 (s, C-*C*^{Ph}), 131.1 (d, $J_{P,C}=2.7$, Hz C-*C*^{Ph}), 131.6 (d, $J_{P,C}=9.2$, Hz C-*C*^{Ph}), 132.0 (d, $J_{P,C}=7.0$, Hz C-*C*^{Ph}), 136.9 (d, $^{2}J_{P,C}=6.4$ Hz C-*C*$^{ipso-Ph}$), 139.3 (d, $^{2}J_{P,C}=6.4$ Hz, C-*C*$^{ipso-Ph}$), 141.9 (d, $^{2}J_{P,C}=8.5$ Hz C-*C*$^{ipso-Ph}$), 149.5 (d, O-*C*=O, $^{2}J_{P,C}=12.1$ Hz), 151.0 (d, P-*C*=N, $^{1}J_{P,C}=8.1$ Hz), 195.6 (dSat, $^{2}J_{P,C}=6.2$ Hz, $^{1}J_{W,C}=126.8$, *cis*-CO), 197.4 ppm (d, $^{2}J_{P,C}=34.1$ Hz, *trans*-CO); ^{31}P NMR (C_6D_6): $\delta=128.07$ ppm, $^{1}J_{W,P}=274.6$ Hz. MS (EI, 184W): *m/z* (%):768.1, $[M]^+$ (5); 740.1, $[M]^+-CO$ (2); 712.1, $[M]^+-2$×CO (10); 684.1, $[M]^+-3$×CO (1); 712.1, $[M]^+-2$×CO (10); 684.1, $[M]^+-3$×CO (2); 640.1, $[M]^+-CO_2-3$×CO, (10); 584.1, $[M]^+-CO_2-5$×CO, (25); 243, $[CPh_3]^+$ (100); IR (ATR): $\tilde{\nu}=2929$ (b, ν-CH$_2$), 2076 (s, ν-CO), 1992 (s, ν-CO), 1930 (s, ν-CO), 1774 (s, ν-CO), 1723 (s, ν-C=O), 1640 cm^{-1} (b, ν-C=N); elemental analysis calcd (%) for $C_{32}H_{29}N_2O_7PW$: C 50.02, H 3.80, N 3.65; found: C 49.80, H 4.17, N 3.50.

CCDC 1056188 (**1a**), 1056102 (hydrolysis product of **1a**), 1056103 (**4**), and 1056104 (**5**) 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.

Computational details

DFT calculations were performed with the ORCA program.[20] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, using the B3LYP functional[21] together with the def2-TZVP basis set.[22] For W atoms the [SD(60,MWB)] effective core potential[23] (ECP) was used. The latest Grimme's semiempirical atom-pair-wise London dispersion correction (DFT-D3) was included in all calculations.[24] Solvent effects (toluene) were taken into account via the COSMO solvation model.[25] Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. From these optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP basis set.[26] Reported energies were corrected for the zero-point vibrational term at the optimization level. Final energies were obtained by means of the recently developed near-linear scaling domain-based local pair natural orbital (DLPNO) method[14] to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)). For the sake of comparison, energy values were also obtained with local correlation schemes of type LPNO (local pair natural orbital) for high-level single-reference methods, such as CEPA (coupled electron-pair approximation),[16b,c] here the slightly modified NCEPA/1 version implemented in ORCA was used,[16a] the spin component scaled (SCS) Moeller-Plesset MP2 level[27] and Grimme's Double-hybrid-meta-GGA functional PWPB95[15] together with D3 correction (PWPB95-D3). Energy values were corrected for the BSSE (basis set superposition error) using the counterpoise method[28] at the $\mathbf{1c}^{\boldsymbol{E}}\cdot CO_2$ stage. Wiberg bond indices (WBI) were obtained from the natural bond orbital (NBO) population analysis.[29] Bader's AIM-derived topological analysis of the electron density was conducted with AIM2000.[30] The NCIplot in Figure 3 of the main text was obtained using the wave function (electron density) at the B3LYP/def2-TZVPPecp level and drawn with VMD.[31]

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[1] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[2] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81.

[3] a) D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136; b) A. Stute, G. Kehr, R. Frohlich, G. Erker, *Chem. Commun.* **2011**, *47*, 4288–4290; c) C. Rosorius, G. Kehr, R. Frohlich, S. Grimme, G. Erker, *Organometallics* **2011**, *30*, 4211–4219; d) F. Bertini, F. J. J. de Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2012**, *134*, 201–204; e) E. J. Lawrence, V. S. Oganesyan, D. L. Hughes, A. E. Ashley, G. G. Wildgoose, *J. Am. Chem. Soc.* **2014**, *136*, 6031–6036.

[4] a) C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2011**, *50*, 3925–3928; *Angew. Chem.* **2011**, *123*, 4011–4014; b) G. Ménard, L. Tran, J. S. J. McCahill, A. J. Lough, D. W. Stephan, *Organometallics* **2013**, *32*, 6759–6763; c) W. Uhl, P. Wegener, M. Layh, A. Hepp, E. Würthwein, *Organometallics* **2015**, DOI: 10.1021/om501206p.

[5] For some recent examples, see: a) C. Murcia-García, A. Bauza, G. Schnakenburg, A. Frontera, R. Streubel, *Cryst. Eng. Comm.* **2015**, *17*, 1769–1772; b) M. Klein, C. Albrecht, G. Schnakenburg, R. Streubel, *Organometallics* **2013**, *32*, 4938–4943; c) J. M. Villalba Franco, A. Espinosa Ferao, G. Schnakenburg, R. Streubel, *Chem. Commun.* **2013**, *49*, 9648–9650; d) R. Streubel, J. Fassbender, G. Schnakenburg, A. Espinosa Ferao, **2015**, submitted.

[6] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 4792–4795; *Angew. Chem.* **2012**, *124*, 4876–4885.

[7] a) T. P. M. Goumans, A. W. Ehlers, K. Lammertsma, E.-U. Würthwein, *Eur. J. Org. Chem.* **2003**, 2941–2946; b) J. C. Slootweg, M. J. M. Vlaar, D. J. Vugts, T. Eichelsheim, W. Merhai, F. J. J. de Kanter, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2005**, *11*, 4808–4818.

[8] a) H. Quast, E. Schmitt, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 381–382; *Angew. Chem.* **1970**, *82*, 395–396; b) H. Quast, S. Aldenkortt, B. Freudenreich, P. Schäfer, M. Hagedorn, J. Lehmann, K. Banert, *J. Org. Chem.* **2007**, *72*, 1659–1666.

[9] M. Seidl, C. Kuntz, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 2771–2775; *Angew. Chem.* **2015**, *127*, 2810–2814.

[10] J. M. Villalba Franco, T. Sasamori, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Chem. Commun.* **2015**, *51*, 3878–3881.

[11] Exchange reactions of a π-system at a phosphorus center are extremely rare; for selected examples, see: a) H. Wilkens, J. Jeske, P. G. Jones, R. Streubel, *Chem. Commun.* **1997**, 2317–2318; b) R. Streubel, U. Schiemann, P. G. Jones, N. H. T. Huy, F. Mathey, *Angew. Chem. Int. Ed.* **2000**, *39*, 3686–3688; *Angew. Chem.* **2000**, *112*, 3845–3847; c) M. J. M. Vlaar, S. G. A. van Assema, F. J. J. De Kanter, M. Schakel, A. L. Spek, M. Lutz, K. Lammertsma, *Chem. Eur. J.* **2002**, *8*, 58–65; d) N. E. Brasch, I. G. Hamilton, E. H. Krenske, S. B. Wild, *Organometallics* **2004**, *23*, 299–302.

[12] The hydrolysis products possess ^{31}P{^{1}H} resonances (THF) at 91.2 ppm ($^{1}J_{WP}=284.2$ Hz; from **1a**) and 90.7 ppm ($^{1}J_{WP}=283.7$ Hz; from **1b**); the corresponding *N*-isopropyl derivative was isolated and completely characterized (see the Supporting Information).

[13] Besides the reference DLNPO-CCSD(T)/def2-TZVPP high computational level,[14] some other levels were checked (see the Supporting Information); according to their root-mean-square deviation (rmsd), a remarkable agreement was obtained, particularly in case of LNPO-NCEPA/1[15] (rmsd 0.17 kcal mol^{-1}) and PWPB95-D3[16] (rmsd 0.60 kcal mol^{-1}) with the same basis set.

[14] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.* **2013**, *139*, 134101.

[15] a) L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **2011**, *7*, 291–309; b) L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.

[16] a) F. Wennmohs, F. Neese, *Chem. Phys.* **2008**, *343*, 217–230; b) F. Neese, F. Wennmohs, A. Hansen, *J. Chem. Phys.* **2009**, *130*, 114108; c) F. Neese, A. Hansen, F. Wennmohs, S. Grimme, *Acc. Chem. Res.* **2009**, *42*, 641–648.

[17] NCIplot, version 1.2. Department of Chemistry, Duke University (USA), 2011. http://www.chem.duke.edu/~yang/Software/software NCI.html; a) E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras García, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 6498–6506; b) J. Contreras García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan, W. Yang, *J. Chem. Theory Comput.* **2011**, *7*, 625–632. Here, λ_2 stands for the second highest eigenvalue of the electron density Hessian matrix. Based on electron density and its derivatives, represents in real space regions with electron density regime below that for typical covalent bonds and ranging from strong or moderate NCIs (blue; for example, hydrogen bonds), weak interactions (green; for example, van der Waals interactions) and steric (repulsive) clashes (red).

[18] A similar RSE of 50.49 kcal mol^{-1} is found at the current DLPNO-CCSD(T) level.

[19] A. Bauzá, D. Quiñonero, P. M. Deyà, A. Frontera, *Chem. Phys. Lett.* **2012**, *536*, 165–169.

[20] ORCA - An ab initio, DFT, and semiempirical SCF-MO package. Written by F. Neese, Max Planck Institute for Bioinorganic Chemistry, 45470 Mül-

heim/Ruhr, 2012. Version 3.0.2. Webpage: http://www.cec.mpg.de/forum/portal.php F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

[21] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[22] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[23] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141. ECP basis sets for W [SD(60,MWB)] have been obtained from Turbomole basis set library at ftp://ftp.chemie.uni-karlsruhe.de/pub/basen/.

[24] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[25] a) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799–805; b) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235.

[26] A. Bergner, M. Dolg, W. Kuchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431–1441. Obtained from the EMSL Basis Set Library at https://bse.pnl.gov/bse/portal. D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571–1586.

[27] a) S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095–9102; b) S. Grimme, L. Goerigk, F. F. Reinhold, *WIREs Comput. Mol. Sci.* **2012**, *2*, 886–906.

[28] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.

[29] Using the NBO 5.9 code. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold„ Theoretical Chemistry Institute, University of Wisconsin, Madison (**2001**).

[30] AIM2000 v. 2.0, designed by F. Biegler-König and J. Schönbohm. 2002. Homepage: http://www.aim2000.de/. a) F. Biegler-König, J. Schönbohm, D. Bayles, *J. Comput. Chem.* **2001**, *22*, 545–559; b) F. Biegler-König, J. Schönbohm, *J. Comput. Chem.* **2002**, *23*, 1489–1494.

[31] VMD—Visual Molecular Dynamics. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics* **1996**, *14*, 33–38. Homepage: http://www.ks.uiuc.edu/Research/vmd/.

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