Facile Synthesis of a Stable Side-on Phosphinyne Complex by Redox Driven Intramolecular Cyclisation

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1. **EPR measurement of intermediate (IM1)$_2^{2+}$**

The X-band EPR spectrum was recorded on a Bruker EMX CW-micro spectrometer equipped with an ER 4131VT Digital Temperature Control System and an ER 4119HS-WI high-sensitivity optical resonator. The calibration of the $g$ value was performed using DPPH (2,2diphenyl-1-picrylhydrazyl) ($g = 2.0036 \pm 0.00004$). A sample of the reaction mixture of 3c with Jutzi acid in CH$_2$Cl$_2$ was filled into a J. Young EPR tube under inert conditions and measured 90 minutes after the start of the reaction at 300 K. Analysis of the hyper fine coupling was performed using the simulation program EPRsim32.^[S1]\]

![Figure S1](image.png)

**Figure S1.** X-band EPR spectrum of reaction mixture 3c with [H(Et$_2$O)$_2$][(B(C$_6$F$_5$)$_4$] at 300 K after 90 min; black = experiment, red = simulation with $g_{iso} = 2.003$; hyperfine coupling to $^{127}$I ($S = 5/2$, 100%) with $A_{iso} = 25 \times 10^{-4}$ cm$^{-1}$. Hyperfine coupling to $^{183}$W was not accounted for because of restricted resolution.

2. **Cyclic voltammetry and spectro-electrochemical measurements**

Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 3. A three electrode arrangement with a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl in CH$_3$CN reference electrode and 0.15 M $^6$Bu$_4$NPF$_6$ as supporting electrolyte was employed. The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as internal standard.
Figure S2. Cyclic voltammetry of complex 3c (black) and 3d (red) measured in CH$_2$Cl$_2$ (referenced against ferrocene/ferrocenium). 3c shows a reversible oxidation at $E_{1/2} = +0.011$ V. 3d shows a reversible oxidation at $E_{1/2} = +0.38$ V. Both are putative W$^{III}$/W$^{II}$ redox process. [S2]

Spectro-electrochemical data were also acquired with a Princeton Applied Research VersaSTAT 3 potentiostat. The optically transparent thin-layer electrochemical (OTTLE) cell was home-built. It comprised a Pt working and counter electrode and a thin silver wire as a pseudoreference electrode sandwiched between two CaF$_2$ windows of a conventional liquid IR cell. The working electrode was positioned in the centre of the spectrometer beam. The build-up followed the design of Hartl and co-workers and modifications of Winter et al. [S3]

Figure S3. IR spectro-electrochemical measurement of 3c. Changes of the spectra during oxidation (left) and reduction (right) shows reversible W(II)/W(III) oxidations steps. The CO vibration increases from 1923 cm$^{-1}$ to 2085 cm$^{-1}$
3. Crystallographic Details

Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fibre. During the measurement the samples were cooled to 173(2) K. Diffraction data were collected on a Bruker-Nonius Apex X8, Bruker D8 Quest- diffractometer and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Structure solutions were found by direct methods (SHELXS-97)[S4] and were refined by full-matrix least-squares procedures on $F^2$ (SHELXL-97).[S5] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at calculated positions with fixed thermal parameters.

![Figure S4. Molecular crystal structure of the complex 3a (left) and 3b (right) (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): 3a: P1-C2 1.811(3), C1-C2 1.314(5), C1-C4 1.516(4), W1-C1 2.043(3), W1-C2 2.063(3), W1-C3 1.971(3), C2-C1-C4 141.2(3), C1-C2-P1 134.0(3). 3b: W1-C1 2.063(4), W1-C2 2.067(4) P1-C1 1.795(4), C1-C2 1.316(5), C2-C16 1.529(5), O2-C16 1.452(5), C2-C1-P1 141.3(3), C1-C2-C16 142.2(4).]
**Figure S5.** Molecular crystal structure of the complex 3c (left) and 3d (right) (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **3c**: P1-C1 1.785(3), C1-C2 1.309(4), C2-C16 1.515(4), W1-C2 2.055(3), W1-C1 2.059(2), P1-C16 3.866, W1-C3A 1.972(3), W1-C2 2.055(3), W1-C2 2.059(2), C2-C1-P1 141.0(2), C1-C2-C16 140.3(2). **3d**: P1-C1 1.805(3), C1-C2 1.322(4), C2-C15 1.510(4), W1-C1 2.046(3), W1-C2 2.048(3), W1-C28 1.975(3), W1-C29 2.132(3), C2-C1-P1 136.0(2), C1-C2-C15 139.0(3).

**Figure S6.** Molecular crystal structure of the complex 4a (left) and 4b-(B(C6F5)4) (right) (50% thermal ellipsoids). Hydrogen atoms and the anion (B(C6F5)4) of 4b+ have been omitted for clarity. Selected bond lengths (Å) and angles (°): **4a**: P1 C1 1.795(4), C1-C2 1.322(6), C2-C16 1.468(5), C16-C21A 1.336(17), C16-C17A 1.510(15), C2-C1-P1 129.7(3), C1-C2-C16 136.5(4). **4b+**: P1-C1 1.7440(18), P1-C28 1.7864(18), C23-C28 1.405(2), C16-C23 1.537(2), C2-C16 1.502(2), C1-C2 1.332(2), C2-C16-C17 117.21(14), C2-C16-C23 112.34(14), C17-C16-C23 114.06(14).
Figure S7. Molecular crystal structure of the complex 4c-OTf (left) and 5 (right) (50% thermal ellipsoids). Hydrogen atoms and the anion CF$_3$SO$_3^-$ of 4c$^+$ have been omitted for clarity. Selected bond lengths (Å) and angles (°): 4c$^+$: P1-C1 1.753(4), P1-C28 1.808(4), C23-C28 1.386(7), C16-C23 1.517(7), C2-C16 1.501(6), C1-C2 1.341(6), C2-C16-C17 124.8(4), C2-C16-C23 107.0(3), C23-C16-C17 103.4(4). 5: C1-P1 1.743(10), P1-C28 1.772(10), C28-C23 1.395(15), C23-C16 1.426(15), C16-C2 1.401(13), C2-C1 1.383(13), C2-C16-C17 135.4(10), C2-C16-C23 116.3(9), C23-C16-C17 108.1(9).
### Table S1. Crystallographic details for 3a, 3b and 3c.

| compound | 3a                | 3b                | 3c                |
|----------|-------------------|-------------------|-------------------|
| empirical formula | C_{39}H_{49}BIN_{6}O_{2}PW | C_{46}H_{47}BIN_{6}O_{2}PW, CH_{2}Cl_{2} | C_{46}H_{47}BIN_{6}O_{2}PW, CH_{2}Cl_{2} |
| fw (g mol⁻¹) | 986.37            | 1070.44           | 1153.35           |
| cryst. syst. | monoclinic        | monoclinic        | monoclinic        |
| space group | P 21/c            | P 21/n            | P 21/n            |
| a (Å)      | 10.2536(4)        | 13.1608(5)        | 12.2877(11)       |
| b (Å)      | 17.1296(6)        | 21.0700(8)        | 22.488(2)         |
| c (Å)      | 22.4554(8)        | 15.4408(6)        | 16.4961(15)       |
| α (deg)    | 90                | 90                | 90                |
| β (deg)    | 95.807(2)         | 96.349(2)         | 95.703(4)         |
| γ (deg)    | 90                | 90                | 90                |
| V(Å³)      | 3923.8(2)         | 4255.4(3)         | 4535.8(7)         |
| Z          | 4                 | 4                 | 4                 |
| T (K)      | 123(2)            | 123(2)            | 123(2)            |
| ρ (g cm⁻³) | 1.670             | 1.671             | 1.689             |
| μ (mm⁻¹)   | 3.813             | 3.524             | 3.427             |
| measured reflns | 122203           | 136838            | 85175             |
| indep reflns | 14207           | 12426             | 16405             |
| reflns with I>2σ(I) | 11122            | 9085              | 12434             |
| Rint       | 0.0862            | 0.1393            | 0.0674            |
| R1 (F[I>2σ(I)]) | 0.0433           | 0.0449            | 0.0348            |
| wR2 (F²[all data]) | 0.0759          | 0.0673            | 0.0656            |
| GOF        | 1.074             | 1.040             | 1.030             |
| params     | 473               | 533               | 595               |
| CCDC no.   | 1953264           | 1953265           | 1953270           |
**Table S2.** Crystallographic details for 3d, 4a and 4b-BC$_{24}$F$_{20}$.

| compound          | 3d                  | 4a          | 4b-BC$_{24}$F$_{20}$ |
|-------------------|---------------------|-------------|----------------------|
| empirical formula | $\text{C}_{47}\text{H}_{47}\text{BN}_{7}\text{O}_2\text{PW}$, 1.895(CH$_2$Cl$_2$) | $\text{C}_{40}\text{H}_{40}\text{BIN}_{6}\text{OPW}$, C$_2$BF$_{20}$, 2.5(C$_7$H$_8$) |  |
| fw (g mol$^{-1}$) | 1128.30             | 968.35      | 1962.81              |
| cryst. syst.      | triclinic           | monoclinic  | triclinic            |
| space group       | P -1                | P 21/c      | P -1                 |
| $a$ (Å)           | 11.744(3)           | 10.3946(2)  | 14.8637(15)          |
| $b$ (Å)           | 14.411(3)           | 17.0819(5)  | 16.0601(16)          |
| $c$ (Å)           | 15.520(4)           | 22.0539(6)  | 18.2456(18)          |
| $\alpha$ (deg)   | 92.018(5)           | 90          | 72.666(4)            |
| $\beta$ (deg)    | 100.353(6)          | 96.4260(10) | 77.615(4)            |
| $\gamma$ (deg)   | 108.841(5)          | 90          | 86.467(5)            |
| $V$(Å$^3$)        | 2433.2(9)           | 3891.28(17) | 4060.9(7)            |
| $Z$               | 2                   | 4           | 2                    |
| $T$ (K)           | 123(2)              | 123(2)      | 123(2)               |
| $\rho$ (g cm$^{-3}$) | 1.540              | 1.653       | 1.605                |
| $\mu$ (mm$^{-1}$) | 2.661               | 3.842       | 1.920                |
| measured reflns  | 14872               | 123568      | 34575                |
| indep reflns     | 14872               | 12254       | 29362                |
| reflns with $I$>2$\sigma$(I) | 11405           | 9076        | 25511                |
| $R_{int}$        | 0.0415              | 0.1076      | 0.0524               |
| $R1$ (F[I$>$2$\sigma$(I)]) | 0.0378            | 0.0398      | 0.0288               |
| wR2 (F$^2$[all data]) | 0.0812           | 0.0703      | 0.0722               |
| GOF              | 0.978               | 1.081       | 1.018                |
| params           | 610                 | 506         | 1124                 |
| CCDC no.         | 1953266             | 1953267     | 1953268              |
Table S3. Crystallographic details for 4c-\(\text{CF}_3\text{O}_3\text{S}\) and 5.

|                | 4c-\(\text{CF}_3\text{O}_3\text{S}\) | 5                |
|----------------|-------------------------------------|------------------|
| empirical formula | \(\text{C}_{46}\text{H}_{46}\text{BIN}_6\text{OPW}^+, \text{CF}_3\text{O}_3\text{S}, 2(\text{CH}_2\text{Cl}_2)\) | \(\text{C}_{46}\text{H}_{46}\text{BIN}_6\text{OPW}\) |
| fw (g mol\(^{-1}\)) | 1370.34                             | 1050.41          |
| cryst. syst.    | triclinic                           | orthorhombic     |
| space group     | P -1                                | P 2 1 2 1 2 1    |
| \(a\) (Å)       | 13.5287(12)                         | 11.2493(9)       |
| \(b\) (Å)       | 15.6907(12)                         | 19.2031(15)      |
| \(c\) (Å)       | 15.7435(15)                         | 19.9323(14)      |
| \(α\) (deg)     | 96.623(3)                           | 90               |
| \(β\) (deg)     | 113.751(3)                          | 90               |
| \(γ\) (deg)     | 113.833(2)                          | 90               |
| \(V\) (Å\(^3\))| 2639.2(4)                           | 4305.8(6)        |
| \(Z\)           | 2                                   | 4                |
| \(T\) (K)       | 123(2)                              | 123(2)           |
| \(ρ\) (g cm\(^{-3}\)) | 1.724                              | 1.620            |
| \(μ\) (mm\(^{-1}\)) | 3.106                             | 3.479            |
| measured reflns | 81351                               | 6844             |
| indep reflns    | 11037                               | 6844             |
| reflns with \(I\rangle 2σ(I)\) | 9145                                | 5536             |
| \(R_{int}\)    | 0.0833                              | 0.0564           |
| \(R1\) (\(|F|>2σ(F)\))  | 0.0340                              | 0.0505           |
| \(wR2\) (\(|F|^2[all\ data]\)) | 0.0680                            | 0.1156           |
| GOF             | 1.053                               | 1.027            |
| params          | 777                                  | 525              |
| CCDC no.        | 1953271                             | 1953269          |
4. Multicomponent mixture spectra analysis with multivariate curve resolution

4.1. Reaction of 3c with [H(Et₂O)₂][B(C₆F₅)₄]

For the reaction monitoring via IR spectroscopy complex 3c (83.3 mg, 78 µmol) was solved in CH₂Cl₂ (20 mL) and tempered to 20 °C. The stirred reaction mixture was treated with [H(Et₂O)₂][B(C₆F₅)₄] (65 mg, 78 µmol) solved in CH₂Cl₂ (1.5 mL). The reaction mixture was pumped continuously through the IR cell during the addition. A measurement was taken every 30 seconds, with one measurement being the mean of 8 scans. These results in a series of spectra on a (time × wavenumber) grid from which information about concentration profiles and pure component spectra can be obtained by multivariate curve resolution methods.

For the chemometric analysis of this multicomponent spectral data a kinetic hard-model approach was applied.\textsuperscript{[56]} A large number of possible reaction mechanisms were analysed (Scheme S2). The reaction orders are optimized within the interval [1,2] if no specifications are given by the assumptions about the reaction system. This can cause broken orders. The results of all reaction mechanisms in Scheme S2 were compared with respect to the reconstruction error of the spectral data and the error of the kinetic model fit. Among all tested reaction mechanisms the one in Scheme S1 leads to optimal results.

![Scheme S1. A reaction mechanism for which optimal reaction rates in terms of small reconstruction and model fit errors can be determined.](image-url)

\textbf{Scheme S1.} A reaction mechanism for which optimal reaction rates in terms of small reconstruction and model fit errors can be determined.
Scheme S2. Analysed reaction mechanism for the reaction of 3c with Jutzi acid. The model with best fit is marked. The integration of a species X, which due to its low concentration does not appear as an
independent band in the IR spectrum, does not lead to a reduction of errors in the kinetic hard-model approach.

4.2. Reaction of 3d with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$]

For the reaction monitoring via IR spectroscopy complex 3d (30 mg, 31 µmol) was solved in CH$_2$Cl$_2$ (17 mL) and tempered to 20 °C. The stirred reaction mixture was treated with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] (26 mg, 31 µmol) solute in CH$_2$Cl$_2$ (1.5 mL). The reaction mixture was pumped continuously through the IR cell during the addition. A measurement was taken every 30 seconds, with one measurement being the mean of 8 scans. Again this results in a series of spectra on a (time × wavenumber) grid.

The series of spectra was split into two separate date sets. One covers the range for CO vibration around 1950 cm$^{-1}$ and the other the range for the less sensitive CN vibration above 2100 cm$^{-1}$. Both data sets were analysed with the peak group analysis.[S7] Pure component spectra and concentration profile have been extracted, see Figure S8. Every CN band can be assigned to a CO band, so that the formation of a W$^{III}$-species at around 2083 cm$^{-1}$ can be excluded. It is important to remark that without further assumptions only qualitative but no quantitative concentration-time curves can be obtained by the peak group analysis. Nevertheless, an approximate trend can be extracted. This is shown in particular by the profile for 1933 cm$^{-1}$ (red) and 1992 cm$^{-1}$ (blue) which must be zero from a chemical point of view.

![Figure S8. Decompositions of the mixture spectra of the reaction of 3d with Jutzi acid into the pure component spectra (left) and the corresponding concentration profiles (right). At the top the area around 1950 cm$^{-1}$ is shown, while at the bottom the area over 2100 cm$^{-1}$ is presented.](image)

The unusually broad band at 1976 cm$^{-1}$ and the corresponding bands at 2106 cm$^{-1}$/2138 cm$^{-1}$, which formed immediately after the addition of the acid, seem conspicuous. The reason for this is the cyanide ligand, which besides the phosphine can also bind the proton, which leads to two isomers.[S8] The analysis clearly confirms that there was no complete oxidation of the tungsten centre. Instead the positive charge is stabilized by mesomerism between the ligand and the metal. This enables a significantly durable
intermediate with bands at 1992 cm\(^{-1}\) and 2187 cm\(^{-1}\). The product has a CO vibration at 1944 cm\(^{-1}\) and forms slowly over a period of several days.

It is possible to apply another multivariate curve resolution method, namely a kinetic hard-modelling approach from Section 4.1 for the area around 1950 cm\(^{-1}\). The model in Scheme S3 is used. In comparison to the reaction of 3c with Jutzi acid it does not contain a dead-end but an equilibrium between the long-lived intermediate \(C_{CN}\) and the product \(D_{CN}\).

\[
\begin{align*}
A_{CN} + H^+ & \rightarrow B_{CN} & \text{1. Ord.} & \rightarrow C_{CN} & \text{1. Ord.} & \rightarrow D_{CN} \\
1933 \text{ cm}^{-1} & & 1972 \text{ cm}^{-1} & & 1991 \text{ cm}^{-1} & & 1942 \text{ cm}^{-1}
\end{align*}
\]

Scheme S3. Derived kinetic model for the reaction sequence of 3d with Jutzi Acid.

5. Reaction monitoring with \(^{31}\)P NMR spectroscopy

5.1. Reaction mixture after protonation of 3b with \([\text{H(Et}_2\text{O)}_2][\text{B(C}_6\text{F}_5)_4]\) monitored by \(^{31}\)P NMR spectroscopy

A green solution of 3b (10 mg, 9.4 µmol) in \(\text{CD}_2\text{Cl}_2\) (0.5 mL) in a J. Young NMR tube was treated with \([\text{H(Et}_2\text{O)}_2][\text{B(C}_6\text{F}_5)_4]\) (7.8 mg, 9.4 µmol) solute in \(\text{CD}_2\text{Cl}_2\) (0.2 mL) at -80°C. The upper part of the solution colour changed slowly from green to red. The sample was recorded with 128 Scans at different temperature starting at -80 °C using Bruker Avance 500 MHz (Figure S9). The temperature was increased by 20 K after each measurement. At -40 °C a Proton coupled \(^{31}\)P NMR-spectrum was measured and is shown in Figure S10.

Figure S9. Reaction sequence of 3b with \([\text{H(Et}_2\text{O)}_2][\text{B(C}_6\text{F}_5)_4]\) in \(^{31}\)P NMR spectroscopy. Reaction mixture was heated stepwise from -80 °C to room temperature.
**Figure S10.** $^{31}$P NMR-spectra (top) and $^{31}$P-$^1$H-NMR-spectra (bottom) of the reaction 3b with Jutzi acid at -40 °C. $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta = -3.2$ (d, $J_{PH} = 526.0$ Hz) ppm.

5.2. Reaction mixture after protonation of 3c with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] monitored by $^{31}$P NMR spectroscopy

A green solution of 3c (10 mg, 9.4 µmol) in CD$_2$Cl$_2$ (0.5 mL) in a J. Young NMR tube was treated with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] (7.8 mg, 9.4 µmol) solute in CD$_2$Cl$_2$ (0.2 mL) at -80°C. The upper part of the solution colour changed slowly from green to red. The sample was recorded with 128 Scans at different temperature starting at -80 °C using Bruker Avance 500 MHz (Figure S11). The temperature was increased by 20 K after each measurement. At -80 °C a Proton coupled $^{31}$P NMR-spectrum was measured and is shown in Figure S12.
Figure S11. Reaction sequence of 3c with [H(Et$_2$O)$_2$][(B(C$_6$F$_5$)$_4$)] in $^{31}$P NMR spectroscopy. Reaction mixture was heated stepwise from -80 °C to room temperature. Note the temperature shift of species B from -2.5 ppm at -80 °C to -1.0 ppm at -20 °C.

Figure S12. $^{31}$P NMR-spectra (top) and $^{31}$P-$^1$H-NMR-spectra (bottom) of the reaction 3c with Jutzi acid at -80 °C. $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta = -2.5$ (d, $^1J_{PH} = 501.3$ Hz) ppm.
6. NMR-Spectra

6.1. NMR-spectra of compound 3a

Figure S13. $^1$H NMR of 3a in CDCl$_3$ (*); + CH$_2$Cl$_2$ # Hexane/Pentane

Figure S14. $^{31}$P NMR of 3a in CDCl$_3$
Figure S15. $^{13}$C NMR of 3a in CDCl$_3$ (*# Hexane/Pentane

Figure S16. DEPT135 NMR spectrum of 3a in CDCl$_3$ (*# Hexane/Pentane
6.2. **NMR-spectra of compound 3b**

![NMR Spectra](image)

**Figure S17.** $^1$H NMR of 3b in CD$_2$Cl$_2$ (*); + H$_2$O

**Figure S18.** $^{31}$P NMR of 3b in CD$_2$Cl$_2$. 
Figure S19. $^{13}$C NMR of 3a in CD$_2$Cl$_2$ (*).

Figure S20. DEPT135 NMR spectrum of 3a in CD$_2$Cl$_2$.
6.3. **NMR-spectra of compound 3c**

![Chemical structure of compound 3c](image)

**Figure S21.** $^1$H NMR of 3c in CD$_2$Cl$_2$ (*).

**Figure S22.** $^{31}$P NMR of 3c in CD$_2$Cl$_2$. 

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*S20*
Figure S23. $^{13}$C NMR of 3c in CDCl$_3$ (* # Pentane)

Figure S24. DEPT135 NMR spectrum of 3c in CD$_2$Cl$_2$
6.4. NMR-spectra of compound 3d

Figure S25. $^1$H NMR of 3d in CD$_2$Cl$_2$ (*);# n-pentane.

Figure S26. $^{31}$P NMR of 3d in CD$_2$Cl$_2$. 
Figure S27. $^{13}$C NMR of 3d in CD$_2$Cl$_2$ (* # n-Pentane.

Figure S28. DEPT 135 NMR spectrum of 3d in CD$_2$Cl$_2$ NMR-spectra of compound 4b
6.5. **NMR-spectra of compound 4a**

**Figure S29.** $^1$H NMR of 4a in CDCl$_3$ (*), # CH$_2$Cl$_2$, + Et$_3$N.

**Figure S30.** $^{31}$P NMR of 4a in CDCl$_3$. 
6.6. NMR-spectra of compound \(4b\-[(B(C_6F_5)_4]\)

**Figure S31.** \(^1\text{H} \) NMR of \(4b\-[(B(C_6F_5)_4]\) in CD\(_2\)Cl\(_2\) (*) , # toluene, + impurity

**Figure S32.** \(^{31}\text{P} \) NMR of \(4b\-[(B(C_6F_5)_4]\) in CD\(_2\)Cl\(_2\).
Figure S33. $^{13}$C NMR of 4b-[B(C$_6$F$_5$)$_4$] in CDCl$_3$ (* # impurity)

Figure S34. DEPT135 NMR spectrum of 4b-[B(C$_6$F$_5$)$_4$] in CDCl$_3$
6.7. **NMR-spectra of compound 4c-OTf**

**Figure S35.** $^1$H NMR of 4c-OTf in CD$_2$Cl$_2$ (*); + Et$_2$O # impurity

**Figure S36.** $^{31}$P NMR of 4c-OTf in CD$_2$Cl$_2$
Figure S37. $^{13}$C NMR of 4c-OTf in CD$_2$Cl$_2$ (*)

Figure S38. DEPT135 NMR spectrum of 4c-OTf in CD$_2$Cl$_2$
Figure S39. $^{19}$F NMR of 4c-OTf in CD$_2$Cl$_2$.

6.8. NMR-spectra of compound 5

Figure S40. $^1$H NMR of 5 CDCl$_3$ (*), # CH$_2$Cl$_2$, + impurity
Figure S41. $^{31}$P NMR of 5 in CDCl$_3$.

Figure S42. $^{13}$C NMR of 5 in CDCl$_3$ (∗) + impurity
The calculations were carried out using either the G09RevE.01\textsuperscript{[9]} or the ORCA 4.11\textsuperscript{[10]} program package applying DFT. The molecular geometries of complex cation 4c\textsuperscript{+} and neutral 5 as well as of the potential intermediates IM1\textsuperscript{+} (open-shell triplet and closed shell singlet), syn-IM2\textsuperscript{+} and anti-IM2\textsuperscript{+} (which were not isolated) were optimized without truncation and symmetry constraints in the gas phase using either the PBE0 functional\textsuperscript{[11]} or the long-range corrected CAM-b3lyp\textsuperscript{[12]} Quasi-relativistic effective core potentials of the Stuttgart/Cologne group were used for W (ECP60) and I (ECP46) in combination with (8s7p6d2f1g)/[6s5p3d2f1g] basis set for W and a (4s5p)/[2s3p] basis set for I.\textsuperscript{[13]} Split valence triple \(\zeta\)-basis sets (def2-TZVP) of the Ahlrich group were used for the other elements.\textsuperscript{[14]} Dispersion was accounted for by the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).\textsuperscript{[15]} In doing so a reasonable match between the calculated and the experimentally determined structures for the cyclization product 4c\textsuperscript{+} was achieved. A comparison of calculated and experimentally determined metric parameters for 4c\textsuperscript{+} is given in Table S4. The strongest deviations (1.29 \%, 1.22 \%) arise for the coordinative bonds W–I and W–N with CAM-b3lyp, while most deviations are well below 1 \%. Frequency calculations were performed with a smaller def2-SVP basis set in order to identify...
all stationary points as minima. The final enthalpies ($\Delta H$) were calculated using the total electronic energy from the higher level calculation and the thermal correction to enthalpy from the frequency calculation. TD-DFT calculations for complex 5 and extraction of the difference densities were performed with Orca (Figure S44).

**Table S4.** Comparison of essential bond lengths [Å] for 4c$^+$ obtained by X-ray structure analysis and single molecule geometry optimization in the gas phase, the calculated bond lengths were rounded for clarity.

|          | 4c$^+$ (calc., PBE0) | 4c$^+$ (calc., CAM-b3lyp) | 4c$^+$ (exp. in 4c-OTf) |
|----------|----------------------|---------------------------|-------------------------|
| W1–C1    | 2.002                | 2.006                     | 2.009(4)                |
| W1–C2    | 2.044                | 2.050                     | 2.050(4)                |
| W1–I1    | 2.7894               | 2.8112                    | 2.7773(3)               |
| W1–N1    | 2.259                | 2.274                     | 2.245(3)                |
| W1–N3    | 2.187                | 2.206                     | 2.184(3)                |
| W1–N5    | 2.215                | 2.227                     | 2.221(3)                |
| W1–C3    | 1.981                | 1.997                     | 1.980(4)                |
| C1–C2    | 1.340                | 2.328                     | 1.341(6)                |
| C1–P1    | 1.732                | 1.735                     | 1.753(4)                |
| C2–C16   | 1.489                | 1.492                     | 1.501(6)                |

**Figure S44.** Comparison calculated and experimental absorption spectrum of 5; experimental (black), calculated PBE0 (blue), calculated b3lyp (red); Gaussian line shape with 30 nm peak width, energy shift –16 nm for b3lyp and +31 nm for PBE0.
Natural resonance theory analysis (NRT):

The implementation of NRT to transition metal complexes frequently poses problems, which arise from the orthogonalization procedure for the d-orbitals. The identification of a starting reference resonance structure for complex 5 turned out to be impossible. Hence, a simplified, truncated model complex bearing NH$_3$/NH$_2^-$ ligands was used for the analysis. NBO6, the standard functional b3lyp and a SDD basis set were used. Due to the strong delocalization full density matrix (FDM) and a stabilization threshold of 30 kcal/mol were applied. Nine leading resonance structures for the optimized structure (Figure S45) are depicted in Figure S46.

![Optimized molecular structure of the model phosphinyne complex.](image)

**Figure S45.** Optimized molecular structure of the model phosphinyne complex.

![Leading resonance structures derived from natural resonance theory.](image)

**Figure S46.** Leading resonance structures derived from natural resonance theory.
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -3.582220 | -4.22217  | -1.321570 |
| C       | -2.829426 | -3.109307 | -0.965308 |
| C       | -4.877378 | -4.376747 | -0.852154 |
| C       | -3.400614 | -2.157711 | -1.26736  |
| C       | -5.466752 | -3.417501 | -0.017907 |
| C       | -2.873254 | -0.916989 | 0.386348  |
| C       | -4.729551 | -2.315625 | 0.337268  |
| C       | -1.588671 | -0.404429 | 0.160727  |
| C       | -3.924203 | -0.299354 | 1.173200  |
| C       | -5.054484 | -1.151058 | 1.167243  |
| W       | 0.424084  | -0.766088 | -0.025214 |
| C       | -0.903329 | 0.750816  | 0.060132  |
| C       | -3.957989 | 0.895662  | 1.881202  |
| C       | -6.194986 | -0.812807 | 1.850523  |
| I       | 0.267339  | -1.779283 | -2.60473  |
| N       | 1.737157  | 0.740238  | -0.917299 |
| N       | 2.315034  | -1.951462 | 0.149374  |
| C       | -0.307735 | -2.467511 | 0.817817  |
| P       | -1.221741 | 2.428056  | 0.465620  |
| C       | -2.657679 | 2.903328  | -0.526740 |
| C       | -3.309550 | 4.089508  | -0.184700 |
| C       | -3.169312 | 2.116439  | -1.555604 |
| C       | -4.442156 | 4.488630  | -0.873744 |
| C       | -4.312914 | 2.511177  | -2.232053 |
| C       | -4.948593 | 3.697003  | -1.895381 |
| C       | 0.442677  | 1.640687  | -2.876215 |
| C       | 1.638084  | 1.515799  | -2.012610 |
| C       | 2.839730  | 2.196086  | -2.211044 |
| N       | 2.977145  | 0.932218  | -0.407705 |
| C       | 3.142256  | 3.135149  | -3.321996 |
| N       | 3.444970  | -1.315869 | 0.541116  |
| C       | 2.631246  | -3.253762 | 0.003431  |
| C       | 4.461691  | -2.184732 | 0.639724  |
| C       | 0.140808  | 3.511604  | -0.013533 |
| C       | 0.048605  | 4.448415  | -1.040111 |
| C       | 1.267495  | 3.501374  | 0.809283  |
| C       | 1.085233  | 5.341729  | -1.258157 |
| C       | 2.308403  | 4.381728  | 0.573908  |
| C       | 2.218942  | 5.304362  | -0.459080 |
| C       | -5.112890 | 1.231669  | 2.577756  |
| C       | -6.215971 | 0.391697  | 2.561423  |
| O       | -0.665424 | -3.374611 | 1.405339  |
| N       | 2.427776  | 0.416143  | 1.981005  |

Table S5. Cartesian coordinates of the geometry optimized structures of $^{11}$IMI + in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).
C 0.572060 0.141194 3.075630  C 0.587277 0.005844 3.132110
C 3.981790 -3.441972 0.300807  C 4.124060 -3.289479 0.463553
B 3.427665 0.182533 0.839960  B 3.405873 0.323499 0.894575
C 2.639759 0.924447 3.207596  C 2.533119 1.048076 3.235664
C 1.707079 -4.340269 -0.400370  C 1.922822 -4.311048 -0.300697
C 5.829262 -1.776517 1.043843  C 5.867994 -1.533672 1.241706
B 3.427665 0.182533 0.839960  B 3.405873 0.323499 0.894575
C 2.639759 0.924447 3.207596  C 2.533119 1.048076 3.235664
C 1.707079 -4.340269 -0.400370  C 1.922822 -4.311048 -0.300697
C 5.829262 -1.776517 1.043843  C 5.867994 -1.533672 1.241706
Table S6. Cartesian coordinates of the geometry optimized structures of $\text{IM1}^+$ in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).

| Element | X     | Y    | Z     | Element | X     | Y    | Z     | Element | X     | Y    | Z     |
|---------|-------|------|-------|---------|-------|------|-------|---------|-------|------|-------|
| C       | -3.604881 | -4.377046 | -1.087788 | C       | -3.658476 | -4.306682 | -1.189903 | C       | -2.881553 | -3.208230 | -0.858281 |
| C       | -2.837339 | -3.264727 | -0.773064 | C       | -2.881553 | -3.208230 | -0.858281 | C       | -4.983652 | -4.385556 | -0.790769 |
| C       | -3.417211 | -2.216211 | -0.066040 | C       | -3.441454 | -2.180362 | -0.110386 | C       | -5.561906 | -3.359893 | -0.047727 |
| C       | -2.92095 | -0.937859 | 0.376705  | C       | -2.902134 | -0.917752 | 0.364674  | C       | -4.794204 | -2.270479 | 0.287528  |
| C       | -1.596544 | -0.420588 | 0.189296  | C       | -1.599074 | -0.402816 | 0.172841  | C       | -5.122609 | -1.067669 | 1.052024  |
| C       | -3.971958 | -0.257968 | 1.074066  | C       | -3.968782 | -0.256348 | 1.03583   | W       | 0.444872 | -0.764205 | -0.009142 |
| C       | -5.124878 | -1.076380 | 1.027812  | C       | -5.122609 | -1.067669 | 1.052024  | C       | -0.922080 | 0.736673  | 0.148464  |
| C       | -6.301049 | -0.675674 | 1.623510  | C       | -6.286595 | -0.686277 | 1.675873  | I       | 0.191401 | -0.960500 | -2.483271 |
| N       | 1.712075 | 0.713904 | -0.988315 | N       | 1.718951 | 0.721281 | -0.986024 | N       | 1.261424 | 0.005128 | 1.838707  |
| N       | 2.323141 | -1.958305 | 0.177671  | N       | 2.332541 | -1.952547 | 0.207671  | C       | -0.324233 | -2.351364 | 1.041628  |
| P       | -1.199957 | 2.419477 | 0.516638  | P       | -1.215669 | 2.433298 | 0.537922  | C       | -2.635762 | 2.927545 | -0.454220 |
| C       | -3.231520 | 4.146532 | -0.123080 | C       | -3.293339 | 4.096367 | -0.116597 | C       | -3.205691 | 2.138062 | -1.450124 |
| C       | -4.356385 | 4.574190 | -0.791883 | C       | -4.417744 | 4.511259 | -0.804979 | C       | -4.350689 | 2.562605 | -2.105433 |
| C       | -4.929761 | 3.779889 | -1.780702 | C       | -4.921562 | 3.738206 | -1.838513 | C       | 0.307945 | 1.560752 | -2.884583 |
| C       | 1.548746 | 1.476481 | -2.082642 | C       | 1.582942 | 1.465350 | -2.093664 | C       | 2.730477 | 2.171251 | -2.344496 |
| N       | 2.971977 | 0.922310 | -0.540421 | N       | 2.974620 | 0.935002 | -0.514082 | C       | 2.968902 | 3.104351 | -3.475932 |
| N       | 3.487686 | -1.314741 | 0.426428  | N       | 3.489373 | -1.293338 | 0.477017  |
Table S7. Cartesian coordinates of the geometry optimized structures of syn-IM2 in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).

|   |   |   |   |
|---|---|---|---|
| H | -7.253347 | 0.878248 | 2.759622 | H | -7.218188 | 0.830358 | 2.871842 |
| H | 2.090599 | -5.137390 | -0.747400 | H | 2.166479 | -5.132894 | -0.728507 |
| H | 1.345321 | -5.137390 | -0.747400 | H | 1.399602 | -4.849417 | 0.823913 |
| H | 6.561597 | -2.640256 | 0.965160 | H | 6.571664 | -2.586513 | 0.798926 |
| H | 6.012826 | -1.325501 | 1.738356 | H | 5.993264 | -1.273381 | 1.818993 |
| H | 6.242490 | -1.045595 | 0.013837 | H | 6.250621 | -1.003057 | 0.099869 |
| H | 4.589566 | 0.562357 | 0.965160 | H | 4.599331 | 0.595479 | 1.020606 |
| H | -0.791455 | -1.177954 | 3.527896 | H | -0.803840 | -1.247331 | 3.498782 |
| H | -1.421514 | 0.241376 | 2.683616 | H | -1.448381 | 0.201746 | 2.732203 |
| H | -0.930099 | 0.357921 | 4.371915 | H | -0.950793 | 0.241593 | 4.413012 |
| H | 4.893409 | 0.770537 | 3.471347 | H | 4.842938 | 0.848900 | 3.513129 |
| H | 4.084477 | 2.038093 | 4.393568 | H | 3.990048 | 2.091026 | 4.432203 |
| H | 4.456088 | 2.288235 | 2.683883 | H | 4.368544 | 2.348158 | 2.728199 |
| H | 1.287120 | 0.520027 | 5.931024 | H | 1.210781 | 0.489782 | 5.951458 |
| H | 0.578001 | 2.018699 | 5.332667 | H | 0.511661 | 1.992595 | 5.359534 |
| H | 2.309977 | 1.914612 | 5.613959 | H | 2.236336 | 1.883040 | 5.660490 |
| H | 5.708687 | 1.39932 | -1.21594 | H | 5.721505 | 1.397269 | -1.127101 |
| H | 5.135467 | 2.636111 | -0.098281 | H | 5.124820 | 2.670557 | -0.069591 |
| H | 5.280321 | 2.999309 | -1.820210 | H | 5.316291 | 2.973618 | -1.794426 |
| H | 4.330443 | -5.439870 | 1.037824 | H | 4.356899 | -5.416815 | 1.073724 |
| H | 5.767565 | -6.339200 | 0.420889 | H | 5.801555 | -5.899499 | 0.516115 |
| H | 4.570995 | -5.271706 | -0.698632 | H | 4.652256 | -5.224816 | -0.648968 |
| H | -3.136969 | 1.577356 | 1.854835 | H | -3.127042 | 1.554782 | 1.923745 |

| C | -4.18669 | -4.678728 | 0.461957 | C | -4.167562 | -4.707014 | 0.468408 |
| C | -3.17393 | -3.732614 | 0.348714 | C | -3.172663 | -3.747238 | 0.339711 |
| C | -5.41153 | -4.358884 | 1.036202 | C | -5.388545 | -4.401851 | 1.052568 |
| C | -3.40706 | -2.456808 | 0.832127 | C | -3.420908 | -2.475188 | 0.816727 |
| C | -5.66227 | -3.073714 | 1.501239 | C | -5.652388 | -3.11969 | 1.513782 |
| C | -2.58252 | -1.247491 | 0.837161 | C | -2.609004 | -1.251244 | 0.810529 |
| C | -4.66925 | -2.123557 | 1.398817 | C | -4.670142 | -2.158559 | 1.390850 |
| C | -1.28224 | -0.914141 | 0.338204 | C | -1.303703 | -0.914890 | 0.304930 |
| C | -3.32037 | -0.230495 | 1.386908 | C | -3.343108 | -0.249270 | 1.362014 |
| C | -4.63987 | -0.704317 | 1.727733 | C | -4.660953 | -0.732635 | 1.723153 |
| W | 0.69891 | -0.845769 | -0.154290 | W | 0.688440 | -0.856056 | -0.171659 |
| C | -0.91537 | 0.317894 | -0.078994 | C | -0.936538 | 0.306842 | -0.093625 |
| C | -2.91745 | 1.187929 | 1.576779 | C | -2.943150 | 1.175049 | 1.556542 |
| C | -5.58507 | 0.174040 | 2.132303 | C | -5.602121 | 0.131334 | 2.135646 |
| I | 0.51762 | -1.826333 | -2.750006 | I | 0.523671 | -1.808235 | -2.802960 |
| N | 1.63906 | 1.010924 | -1.023603 | N | 1.640033 | 1.029032 | -1.007622 |
| N | 1.37544 | -0.127677 | 1.800861 | N | 1.346314 | -0.159177 | 1.816715 |
| N | 2.79876 | -1.534489 | -0.091267 | N | 2.806168 | -1.528466 | -0.099796 |
| C | 0.25242 | -2.635099 | 0.575187 | C | 0.277661 | -2.682791 | 0.523648 |
| P | -1.98442 | 1.669634 | 0.057578 | P | -1.993742 | 1.671628 | 0.061424 |
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | -3.13823     | 1.72113      | -1.29776     |
| C    | -4.11072     | 2.721164     | -1.35625     |
| C    | -3.13932     | 0.679419     | -2.224281    |
| C    | -5.06109     | 2.689733     | -2.361552    |
| C    | -4.09776     | 0.657078     | -3.223032    |
| C    | -5.05182     | 1.661343     | -3.294593    |
| C    | 0.11146      | 1.729410     | -2.887185    |
| C    | 1.27143      | 1.874890     | -1.980169    |
| C    | 2.15931      | 2.957362     | -2.933625    |
| C    | 0.340321     | -2.717227    | -0.308394    |
| C    | 4.96823      | -1.247236    | 0.229159     |
| C    | -1.06765     | 3.176150     | 3.064347     |
| C    | -1.24412     | 4.304641     | -0.478967    |
| C    | -0.8079      | 3.155306     | 1.304871     |
| C    | -0.44061     | 5.415307     | 3.073312     |
| C    | 0.71492      | 4.269553     | 1.497354     |
| C    | 0.53553      | 5.397955     | 0.197952     |
| C    | -4.04147     | 2.072815     | 1.987661     |
| C    | -5.25989     | 1.577528     | 2.256504     |
| C    | -0.02177     | -3.655122    | 1.019402     |
| C    | 0.84824      | -0.209951    | 0.854428     |
| C    | 4.77996      | -2.575478    | -0.125535    |
| C    | 2.71810      | -3.981365    | -0.664594    |
| C    | 6.22773      | -0.530670    | 0.546574     |
| B    | 3.42510      | 0.777198     | 0.688528     |
| C    | 2.61734      | 1.119727     | 3.137349     |
| C    | 1.59130      | 0.589158     | 3.910120     |
| C    | -0.31653     | -1.048678    | 3.405907     |
| C    | 3.74559      | 1.949469     | 3.541440     |
| C    | 1.34664      | 0.775454     | 5.366891     |
| C    | 3.08678      | 2.691973     | -1.015645    |
| C    | 4.26521      | 3.485190     | -0.587164    |
| C    | 5.80030      | -3.646110    | -0.284705    |
| H    | -4.01733     | -3.995102    | -0.111201    |
| H    | -2.23089     | 3.984727     | -5.709461    |
| H    | -6.18096     | -5.17296     | -1.11424     |
| H    | -6.62423     | -2.826823    | 1.936029     |
| H    | -6.60021     | -0.146132    | 2.337081     |
| H    | -0.49379     | 0.865172     | -2.642262    |
| H    | 1.79917      | -3.815307    | -1.221816    |
| H    | -4.13554     | 3.513849     | -0.617836    |
| H    | -2.39790     | -0.109904    | -2.168073    |
| H    | -5.81475     | 3.465938     | -2.413600    |
| H    | -4.09742     | -0.150041    | -3.945109    |
Table S8. Cartesian coordinates of the geometry optimized structures of anti-IM2⁺ in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).

|   | C          | C          | C          | C          | C          | C          |
|---|------------|------------|------------|------------|------------|------------|
| H | -3.491591  | -3.517079  | -3.519910  | -3.540999  | -3.580830  | -3.543099  |
| H | -2.694539  | -4.202032  | -4.534009  | -4.543099  | -3.543099  | -4.547533  |
| H | -4.796626  | -5.100506  | -4.543099  | -4.543099  | -4.543099  | -4.547533  |
| H | -3.218222  | -2.942139  | -3.253838  | -3.253838  | -3.253838  | -3.253838  |
| H | -5.347947  | -3.913932  | -5.389334  | -5.389334  | -5.389334  | -5.389334  |
| H | -2.675506  | -1.583088  | -2.703634  | -2.703634  | -2.703634  | -2.703634  |
| H | -4.564140  | -2.818642  | -4.603455  | -4.603455  | -4.603455  | -4.603455  |
| H | -1.358789  | -1.032522  | -1.374688  | -1.374688  | -1.374688  | -1.374688  |
C  -3.709265  -0.703111  -0.142237  C  -3.728775  -0.672748  -0.159852
C  -4.890327  -1.401639  0.300113  C  -4.929306  -1.364359  0.263036
W  0.689360  -0.760714  -0.440967  W  0.681514  -0.768611  -0.440939
C  -1.027648  0.275368  -0.572780  C  -1.034535  0.281221  -0.559499
C  -3.754030  0.758873  -0.381853  C  -3.758675  0.793070  -0.404883
C  -5.978831  0.709918  0.712422  C  -6.012184  0.670191  0.652910
I  1.251342  -1.244860  -3.114096  I  1.223910  -1.243590  -3.145834
N  1.659349  1.254052  -0.686498  N  1.668618  1.259465  -0.668050
N  0.779948  -0.389048  1.721427  N  0.781414  -0.423168  1.741853
C  -2.119356  1.565228  -0.440967  C  -2.122442  1.582562  -0.440939
W  0.689360  -0.760714  -0.440967  W  0.681514  -0.768611  -0.440939
C  5.968779 -3.180190  0.095433  C  5.995499 -3.157458  0.054496
H -3.084514 -6.304132 -0.341952  H -3.107523 -6.270521 -0.289653
H -1.695044 -4.335920 -0.777934  H -1.715901 -4.308244 -0.718510
H -5.393937 -6.076106  0.477872  H -5.432106 -6.036227  0.470359
H -6.378338 -3.829101  0.821357  H -6.424248 -3.790945  0.768056
H -6.853237 -1.222052  1.097558  H -6.897084 -1.173244  1.019910
H -0.032643  1.422921 -2.801498  H  0.019000  1.464321 -2.823074
H  2.267726 -3.431900 -1.686668  H  2.298744 -3.431452 -1.721883
H -1.671540  4.439966  0.153243  H -1.656528  4.458390  0.163335
H -2.649104  1.712304 -3.027636  H -2.597049  1.745371 -3.031423
H -1.792667  6.315455 -1.437406  H -1.742388  6.329629 -1.419771
H -2.815925  3.951618 -4.585670  H -2.725013  3.625799 -4.583935
H -2.373502  5.900767 -3.804164  H -2.285538  5.924256 -3.792404
H  1.388377  1.996523 -3.648936  H  1.463788  2.015767 -3.631636
H  0.241581  3.169630 -2.998850  H  0.325783  3.201707 -3.000298
H  2.788565  5.448389 -1.179821  H  2.885728  5.430323 -1.154716
H  1.273132  5.097483 -2.006501  H  1.354025  5.123595 -1.960277
H  2.803922  4.639816 -2.743096  H  2.859595  4.624874 -2.715159
H  0.212173  2.811920  0.875195  H  0.199205  2.817473  0.919863
H -3.624092  1.503005  2.326040  H -3.639375  1.489352  2.321636
H  0.797239  3.570452  3.140809  H  0.764782  3.543777  3.191472
H -3.008908  2.444229  4.592730  H -3.042550  2.195585  4.594357
H -0.806597  3.266320  5.001693  H -0.849587  3.234747  5.035855
H -4.993521  2.525683  0.136375  H -4.977888  2.562857  0.115179
H -6.858715  1.255805  1.034981  H -6.880132  1.306238  0.967907
H  3.931574 -4.001254 -1.621688  H  3.970123 -3.957839 -1.684278
H  2.815743 -4.426015 -0.327384  H  2.883443 -4.429516 -0.385386
H  6.080795 -0.850186  1.508356  H  6.813473 -0.850519  1.514709
H  5.646335 -0.170241  2.647806  H  5.647120 -0.199202  2.661501
H  6.046295  0.704918  1.171419  H  6.043827  0.701966  1.203590
H  3.797936  1.298452  2.042891  H  3.791367  1.271594  2.074365
H -1.128421 -2.412485  1.933178  H -1.109571 -2.462723  1.937616
H -2.086959 -0.973473  2.261056  H -2.079352 -1.040721  2.291162
H -1.517789 -1.907381  3.592808  H -1.491927 -2.049671  3.600039
H  3.598264  0.571797  4.486097  H  3.593249  0.557725  4.507557
H  2.267076  1.184071  5.465238  H  2.258071  1.130471  5.499050
H  2.860777  2.117844  4.087996  H  2.825034  2.091625  4.134513
H -0.116382 -1.494487  5.587906  H -0.100971 -1.562537  5.601838
H -1.101096 -0.053852  5.345087  H -1.100899 -0.135343  5.365185
H  0.504791  0.081676  6.053163  H  0.498267  0.015600  6.075639
H  4.761712  3.317594  0.926258  H  4.764613  3.296354  1.001771
H  3.417773  3.724046  1.985615  H  3.407680  3.708053  2.037303
H  3.815644  4.773663  0.622617  H  3.835514  4.757249  0.688245
H  5.747193 -4.146255  0.556187  H  5.771362 -4.139634  0.472907
H  6.868946 -2.790392  0.570495  H  6.883230 -2.783447  0.559769
H  6.208898 -3.368789 -0.954379  H  6.254654 -3.302891 -0.995422
H -3.858328  0.874581 -1.478956  H -3.855684  0.899479 -1.498313
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -3.495830  | -5.210900  | -0.174243  |
| C    | -3.453385  | -5.221432  | -0.172357  |
| C    | -2.899891  | -4.036257  | -0.616401  |
| C    | -2.875025  | -4.041866  | -0.618274  |
| C    | -4.388782  | -5.201269  | 0.891715   |
| C    | -4.350874  | -5.217899  | 0.886374   |
| C    | -3.191907  | -2.857630  | 0.041086   |
| C    | -3.190327  | -2.865373  | 0.026878   |
| C    | -4.713190  | -4.015229  | 1.532333   |
| C    | -4.695156  | -4.033633  | 1.516384   |
| W    | 0.664119   | -0.702279  | -0.466919  |
| C    | -1.036238  | 0.349639   | -0.367679  |
| C    | -1.048679  | 0.338967   | -0.371564  |
| C    | -3.309652  | 0.702205   | 1.092493   |
| C    | -3.330778  | 0.691285   | 1.079922   |
| N    | 1.613299   | 1.345250   | -0.559397  |
| C    | 1.608019   | 1.357105   | -0.552460  |
| I    | 0.963068   | -0.602402  | 1.697112   |
| N    | 0.951259   | -0.618968  | 1.708560   |
| W    | 0.659499   | -0.708452  | -0.457826  |
| C    | -0.106555  | -1.065555  | 2.739789   |

Table S9. Cartesian coordinates of the geometry optimized structures of 4c* in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).
Table S10. Cartesian coordinates of the geometry optimized structures of 5 in the gas phase; PBE (left) CAM-b3lyp (right), def2-TZVP/ECP(W, I).

| Atom | X     | Y     | Z     | Atom | X     | Y     | Z     |
|------|-------|-------|-------|------|-------|-------|-------|
| H    | 3.067237 | 1.901051 | 4.036829 | H    | 3.008107 | 1.901382 | 4.074277 |
| H    | 0.396938  | -1.907806 | 5.564708 | H    | 0.401266 | -1.949424 | 5.570701 |
| H    | -0.756550 | 5.407656  | H    | -0.783310 | -0.661489 | 5.406730 |
| H    | 0.853312  | -0.587323 | 5.407656 | H    | 0.783310  | -0.661489 | 5.406730 |
| H    | 4.950040  | 3.094388  | H    | 4.911707 | 3.122635  | 1.006367 |
| H    | 3.718859  | 3.545308  | H    | 3.657771 | 3.560085  | 2.157920 |
| H    | 4.101166  | 4.630843  | H    | 4.057334 | 4.650986  | 0.834303 |
| H    | 5.866146  | -2.41254 | H    | 5.730244 | -4.186483 | -0.28081 |
| H    | 6.844432  | -2.922613 | H    | 6.872661 | -2.867788 | -0.085777 |
| H    | 6.096978  | -3.289221 | H    | 6.167324 | -3.187996 | -1.661355 |

S45
\[ \begin{array}{cccc}
C & -5.306656 & 8.168261 & 3.613079 \\
C & -2.629541 & 6.590176 & 1.490392 \\
C & -2.009181 & 5.352579 & 3.465039 \\
C & -3.351958 & 7.668186 & 6.404185 \\
C & -0.998444 & 7.369621 & 5.956822 \\
C & -3.024417 & 13.183762 & 1.095733 \\
C & -5.004885 & 11.943582 & 1.755104 \\
C & -5.328796 & 10.681177 & 2.390501 \\
H & 3.074258 & 14.109075 & 2.223677 \\
H & 1.585129 & 14.354443 & 3.141288 \\
C & 5.004698 & 11.324638 & 6.267755 \\
C & -3.076454 & 9.494454 & 6.750212 \\
C & -1.673416 & 9.882476 & 8.847356 \\
H & -2.247019 & 12.072260 & 5.028357 \\
H & -2.934290 & 11.841389 & 6.639946 \\
C & 3.549034 & 6.880487 & 6.189170 \\
C & 2.629839 & 5.172349 & 3.576716 \\
H & 0.075569 & 7.842261 & 1.645264 \\
H & 0.465645 & 6.128333 & 1.897801 \\
C & -6.501716 & 8.771743 & 3.257195 \\
C & -5.321664 & 7.171989 & 4.041858 \\
H & -2.913056 & 7.526254 & 1.020371 \\
C & -2.549858 & 5.430228 & 0.740685 \\
C & -1.928816 & 4.193414 & 2.705761 \\
H & -1.804717 & 5.318028 & 4.527861 \\
H & -4.346204 & 7.931051 & 6.063503 \\
C & -3.133083 & 7.345565 & 7.734817 \\
C & -0.787634 & 7.057085 & 7.287976 \\
H & -0.165029 & 7.391651 & 5.265271 \\
H & -1.951130 & 13.300203 & 1.030556 \\
C & -3.855299 & 14.119965 & 0.505126 \\
C & -5.824292 & 12.896560 & 1.163054 \\
C & -6.517622 & 10.028240 & 2.645523 \\
H & 5.260293 & 10.266337 & 6.200979 \\
H & 4.681792 & 11.530647 & 7.292241 \\
H & 5.908644 & 11.902265 & 6.077930 \\
H & 5.234223 & 14.054828 & 3.315386 \\
H & 5.754305 & 13.744683 & 4.968331 \\
H & 4.431898 & 14.865421 & 4.655572 \\
H & 1.687712 & 8.816666 & 8.892358 \\
H & 0.961704 & 10.164131 & 9.779083 \\
H & 2.391266 & 10.422966 & 8.778196 \\
H & -2.001390 & 11.847782 & 8.990700 \\
H & -1.189515 & 10.507104 & 9.798390 \\
\end{array} \]
|   | X   | Y   | Z   |   | X   | Y   | Z   |
|---|-----|-----|-----|---|-----|-----|-----|
| H | -2.571141 | 10.198323 | 8.753981 | H | -2.767351 | 10.2943 | 8.546278 |
| H | 4.310759 | 7.622356 | 6.430184 | H | 4.211039 | 7.569195 | 6.521488 |
| H | 4.051829 | 5.943710 | 5.949991 | H | 3.904813 | 5.921612 | 6.075762 |
| H | 2.953522 | 6.720993 | 7.092818 | H | 2.796714 | 6.772152 | 7.151449 |
| H | 1.734822 | 4.624460 | 3.268619 | H | 1.785908 | 4.625138 | 3.271464 |
| H | 3.077122 | 4.653067 | 4.414174 | H | 3.120180 | 4.657484 | 4.423435 |
| H | 3.334323 | 5.121381 | 2.741089 | H | 3.376010 | 5.148751 | 2.757983 |
| H | -7.434173 | 8.252556 | 3.443452 | H | -7.380704 | 8.268865 | 3.689325 |
| H | -2.775135 | 5.458146 | -0.318818 | H | -2.926673 | 5.412225 | -0.279365 |
| C | -2.200228 | 4.230777 | 1.348414 | C | -2.222275 | 4.213484 | 1.352703 |
| H | -1.664308 | 3.257732 | 3.185848 | H | -1.548305 | 3.272131 | 3.156628 |
| H | -3.965336 | 7.335868 | 8.428869 | H | -3.730573 | 7.271702 | 8.464237 |
| C | -1.853623 | 7.043416 | 8.177098 | C | -1.636294 | 6.976867 | 8.128725 |
| H | 0.213495 | 6.827794 | 7.633564 | H | 0.400656 | 6.755635 | 7.496289 |
| H | -3.414804 | 14.967988 | -0.007099 | H | -3.543160 | 14.978296 | 0.046608 |
| C | -5.245139 | 13.991887 | 0.545096 | C | -5.340478 | 13.992010 | 0.671292 |
| H | -6.902924 | 12.777880 | 1.174356 | H | -6.958354 | 12.772123 | 1.383437 |
| H | -7.463939 | 10.476831 | 2.361527 | H | -7.457249 | 10.466758 | 2.552054 |
| H | -5.869182 | 14.742369 | 0.074266 | H | -5.986052 | 14.752595 | 0.253601 |
| H | -2.146759 | 3.322402 | 0.759813 | H | -2.200172 | 3.300685 | 0.772678 |
| H | -1.685321 | 6.799127 | 9.219726 | H | -1.428465 | 6.707894 | 9.156063 |
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