Supplementary information

Reversible Cooperative Dihydrogen Binding and Transfer with a Bis-Phosphenium Complex of Chromium

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Experimental Procedures

Due to the air and moisture sensitivity of the studied compounds, all manipulations were carried out in flame-dried glassware under an inert gas atmosphere of purified argon. Experiments with H/D2 were carried out in medium-walled valved NMR-Tubes (Norell® extreme series) under an atmosphere of purified gas. Cr(CO)3(naphthalene), Na2[Cr(CO)4], 2-chloro-1,3-bis(2,6-dimethoxyphenyl)-1,3,2-diazaphospholene, 2-hydroxy-1,3-bis(2,6-dimethoxyphenyl)-1,3,2-diazaphospholene and Brookhart’s acid were synthesized as described. THF, n-pentane, n-hexane, benzene and diethyl ether were distilled from Na/K alloy and CH2Cl2 and CH2CN from CaH2 prior to use. C6D6 and THF-D8 were refluxed over NaK alloy for 72 h and CD2CN over CaH2 for 48 h, followed by distillation and storage over molecular sieves in a glovebox. LiHBEt3 (1.0 M solution in THF) was purchased from Sigma Aldrich and used without further purification. Irradiation experiments were carried out with a medium pressure mercury lamp. NMR spectra were acquired on Bruker Avance 250 (1H: 250.0, 13C: 62.9, 31P: 161.9 MHz) or Bruker Avance 400 (1H: 400.1 MHz, 13C: 100.5 MHz, 31P: 161.9 MHz) NMR spectrometers at 293 - 296 K if not stated otherwise. 1H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent (δH = 7.15 (C6D6)). 13C (THF-D8) as secondary reference. NMR Spectra of heteronuclei were referenced using the Z-scale (δH = 25.154052 MHz, 13C, and 85 % 1H). HRMS spectra were recorded with a J&M TIDAS spectrophotometer.

Syntheses

Complex 2

[a] Cr(CO)3(naphthalene) (130 mg, 0.50 mmol) and [b] (100 mg, 1.00 mmol) were dissolved in THF (10 mL). The solution was stirred for 16 h under exclusion of light. The solvent was removed under reduced pressure and the resulting solid suspended in n-pentane (35 mL, 30 min sonication with ultrasound to ensure complete dispersion). Filtration of the suspension over a frit (por. IV), washing the resulting fine orange powder with n-pentane (2 x 20 mL) and drying for 1 h in vacuum gave 250 mg (0.26 mmol, 54 %) of 2.

1H NMR (250 MHz, C6D6): δ = 8.86 (dd, 1H, 3JHH = 341 Hz, 1JHH = 6 Hz, 4JHH = 5.8 Hz, 5JHH = 7.30-7.00 (m, 12 H, C6H12), 6.14 (2 H, 1JHH = 5.9 Hz, NCH), 5.94 (2 H, 1JHH = 6.3 Hz, NCH), 5.99 (sept, 2 H, 1JHH = 6.6 Hz, CH), 5.26 (sept, 2 H, 1JHH = 6.6 Hz, CH), 5.20 (sept, 2 H, 1JHH = 6.6 Hz, CH), 4.00 (6 H, 3JHH = 6.6 Hz, CH), 4.00 (6 H, 3JHH = 6.6 Hz, CH), 1.35 (6 H, 1JHH = 6.0 Hz, CH1), 1.35 (6 H, 1JHH = 6.6 Hz, CH1), 1.25 (6 H, 1JHH = 6.6 Hz, CH1), 1.17 (6 H, 1JHH = 6.6 Hz, CH1), 1.00 (6 H, 1JHH = 6.6 Hz, CH1), -31P NMR (62.9 MHz, C6D6): δ = 222 (br, CO), 149.9 (s, O-C), 149.8 (s, O-C), 147.5 (s, O-C), 138.5 (d, 3JHH = 4.6 Hz, 5JHH = 130.2 (s, p-C), 126.1 (s, NCH), 124.5 (s, m-C), 124.4 (s, m-C), 123.6 (s, m-C), 122.6 (s, NCH), 30.3 (s, CH), 29.2 (s, CH), 28.7 (s, CH), 27.3 (s, CH), 25.3 (s, CH), 25.1 (s, CH), 23.8 (s, CH), 23.6 (s, CH), 23.0 (s, CH), -13C NMR (161.9 MHz, C6D6): δ = 232 (d, 3JHH = 12 Hz), 141 (d, 3JHH = 12 Hz), 13P NMR (161.9 MHz, C6D6): δ = 232 (dd, 3JHH = 12 Hz, 4JHH = 29 Hz, 5JHH = 6 Hz), 141 (dd, 3JHH = 341 Hz, 4JHH = 107 Hz, 5JHH = 12 Hz) - IR (THF): ν = 1992 (s), 1906 (s), 1898 (s) cm⁻¹, ν(CO): 2160 (w) cm⁻¹, ν(PH): ν(C6H4PhCrN3O3P2) (951.17 g mol⁻¹): calc. C 69.31 H 7.83 N 5.62, found C 68.03 H 7.84 N 5.50. - HRMS ([+]+ESI): m/e = 951.4554 ([M+H]⁺), calc. for C6H12CrN3O3P2: 951.4557.

(b) LiHBEt3 (105 μL 1 M solution in THF, 105 μmol) was added to a solution of [Ba(dca)] (100 μmol) in benzene (10 mL) that had been prepared as described below. The solution was stirred for 30 min at 25 °C. A slight fade in color to light orange was observed. The mixture was filtered over diatomaceous earth and the filtrate evaporated to dryness. A mixture of the residual orange solid in n-pentane (10 mL) was sonicated in an ultrasonic bath for 30 min. Filtration over a frit (por. IV) and washing the remaining orange powder with n-pentane (2 x 3 mL) gave analytically pure 2 (32 mg, 30 μmol, 31 %).

Complex 4

A slight optimization of the previously published protocol⁶ was applied. A small amount of THF (0.5 mL) was added at room temperature to a stirred suspension prepared from Na2[Cr(CO)4] (119 mg, 0.50 mmol) and 2-chloro-1,3-bis(2,6-dimethoxyphenyl)-1,3,2-diazaphospholene (440 mg, 1.00 mmol) in n-hexane (10 mL). An immediate color change from clear brown to dark purple accompanied by vigorous gas evolution was observed. The solution was stirred for 30 min until gas formation had ceased. Volatiles were removed under reduced pressure and the resulting topical solid suspended in n-hexane (30 mL). Filtration over diatomaceous earth, concentration of the filtrate to approximate one of the original volume, and storage at -15°C gave 2 as purple crystals (yield 340 mg, 0.35 mmol, 72 %).

1H NMR (THF-D8, 400.1 MHz): δ = 7.25-7.06 (m, 12 H, C6H12), 6.41 (4 H, NCH), 3.24 (sept, 8 H, 1JHH = 6.8 Hz, CH1), 1.12 (24 H, 3JHH = 6.8 Hz, CH1), -13C NMR (62.9 MHz, C6D6): δ = 233 (br, CO), 147.6 (s, O-C), 136.5 (s, i-C), 129.4 (s, p-C), 125.1 (s, NCH), 124.6 (s, m-C), 29.1 (s, CH), 25.5 (s, CH), 23.6 (s, CH). -31P NMR (THF-D8): δ = 240.3 (s). IR (THF): ν = 1963 (s), 1934 (s), 1886 (s) cm⁻¹, ν(CO): ν(C6H4PhCrN3O3P2) (951.15 g mol⁻¹): calc. C 69.45 H 7.65 N 5.89, found C 68.73, H 7.65, N 5.71. - HRMS ([+]+ESI): m/e = 950.4476 ([M+H]⁺), calc. for C6H12CrN3O3P2: 950.4479.
Complex 5[\text{BARf}_4]

A solution prepared from complex 4 (100 mg, 100 \mu mol) and [H(OEt)_2][\text{BARf}_4] (106 mg, 100 \mu mol, Ar' = C_{6}H_{5}(CF_3)_2) in benzene (10 mL) was stirred for 30 min at 25°C. A slow color change from purple to clear orange was observed. Storage at 4°C gave analytically pure 5[\text{BARf}_4] in crystalline form (96 mg, 53 \mu mol, 53 %).

$^1$H NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 5:1, 400.1 MHz): $\delta = 8.22$ (m, 8 H, o-Ar'), 7.64 (m, 4 H, p-Ar'), 7.16 (m, 4 H, C_{6}H_{5}), 7.00 (m, 8 H, C_{6}H_{5}), 6.91 (m, 4 H, NCH), 2.59 (sept, 8 H, $^3$J_{HH} = 6.7 Hz, CH), 1.04 (d, 24 H, $^3$J_{HH} = 6.7 Hz, CH$_3$), 0.95 (d, 24 H, $^3$J_{HH} = 6.7 Hz), -7.94 (t, 1 H, $^3$J_{HH} = 74.9 Hz). $^{13}$C NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 5:1, 100.5 MHz): $\delta = 220.0$ (br, CO), 160.0 (br, i-Ar'), 145.9 (s, o-C), 135.2 (br, o-Ar'), 131.7 (s, NCH), 129.2 (br, m-Ar'), 128.1 (s, p-C), 125.1 (br q, $^3$J_{CH} = 272 Hz, CF$_3$), 125.0 (s, m-C), 117.8 (br, p-Ar'), 29.4 (s, CH), 24.7 (s, CH$_3$), 22.3 (s, CH$_3$). $^{31}$P$^1$H NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 5:1, 161.9 MHz): $\delta = 259.7$ (br). $^{31}$P NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 5:1, 161.9 MHz): $\delta = 259.7$ (d, $^3$J_{PP} = 75 Hz).

Characterization of Complex 3b and isolation of co-crystals of 2/3b.

For spectroscopic characterization of 3b, a solution of complex 2 (20 mg, 20 \mu mol) in \text{CD}_{3}CN/\text{C}_{6}D_{6} (6:1, total volume 0.7 mL) was sonicated in an ultrasonic bath for 15 min. Analysis of the $^1$H NMR spectrum indicated the presence of a 70:30 mixture of 3a and 2. An incomplete set of NMR data of 3b could be determined by analysis of 2D NMR spectra of the equilibrium mixture. Crystals containing an 1:1 mixture of both species suitable for a single-crystal X-ray diffraction study were grown from a solution of 2 (40 mg, 40 \mu mol) in toluene/MeCN (4:1, 18 mL total volume).

3b: $^1$H NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 6:1, 250 MHz): $\delta = 8.62$ (AA'XX'-pattern, $^3$J_{HH} = 277 Hz, $^3$J_{HH} = 2.5 Hz, $^3$J_{HH} = 2.5 Hz, $^3$J_{HH} = 4.5 Hz, 2 H, PH), 7.46-7.07 (m, C_{6}H_{5}), 6.04 (m, 4 H, NCH), 3.77 (sept, 4 H, $^3$J_{HH} = 6.8 Hz, CH), 3.28 (sept, 4 H, $^3$J_{HH} = 6.8 Hz, CH), 1.27 (d, $^3$J_{HH} = 6.8 Hz, CH$_3$), 1.23 (d, $^3$J_{HH} = 6.8 Hz). $^{13}$C NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 6:1, 62.9 MHz): $\delta = 228$ (br, CO), 150.9 (s, o-C), 135.3 (s, i-C), 130.8 (s, p-C), 124.8 (s, m-C), 123.1 (s, NCH), 29.8 (s, CH), 29.4 (s, CH), 27.4 (s, CH$_3$), 25.1 (s, CH$_3$), 24.0 (s, CH$_3$), 23.6 (s, CH$_3$). $^{31}$P$^1$H NMR (\text{CD}_{3}CN/\text{C}_{6}D_{6} 6:1, 161.9 MHz): $\delta = 155.4$ (s).

Reactivity Studies

Thermolysis of 2.

A solution of 2 (13 mg, 13 \mu mol) in \text{C}_{6}D_{6} (0.5 mL) in a valved NMR tube was sonicated by sonification for 10 min and then tempered at 80°C for 12 h. NMR spectra recorded before and after thermolysis revealed conversion of 2 into 4 and H$_2$ (Figure S1).

![Figure S1](image-url)

$^1$H (top) and $^{31}$P$^1$H NMR spectra recorded before (red traces) and after (blue traces) tempering a solution of 2 in \text{C}_{6}D_{6} for 12 h at 80°C. The $^1$H NMR signal at 4.5 ppm is attributable to molecular H$_2$. 4
Thermal reaction of 4 with H₂

A solution of 4 (7 mg, 7 μmol) in THF-D₈ (0.5 mL) was transferred to a medium-walled high pressure NMR tube and degassed by completing three freeze-pump-thaw cycles. The NMR tube was then pressurized with H₂ (8 bar) and kept at 60° C for 300 h. NMR spectra recorded before and after heating showed that trace amounts of 2 had formed (Figure S2).

Photolysis of 4 under H₂, D₂, or a mixture of H₂/HD/D₂.

A solution of 4 (7 mg, 7 μmol) in THF-D₈ (0.5 mL) was transferred to a medium-walled high pressure NMR tube and degassed by completing three freeze-pump-thaw cycles. The NMR tube was then pressurized with the appropriate gas (8 bar H₂, D₂, or a mixture of all isotopomers, respectively) and subsequently irradiated for 7.5 h with a medium pressure mercury lamp. The reaction was monitored by recording NMR spectra before and after the irradiation period (Figures S3 – S9).
Figure S4. $^{31}$P NMR spectrum of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure mercury lamp under 8 bar of H$_2$. Labelled signals are attributable to 4 (triangle), 2 (star), 6 (circle), and 1 (diamond) respectively. Features marked S are electronic spikes and U the signals of unknown by-products.

Figure S5. $^1$H,$^{31}$P-HMQC NMR spectrum and expansions of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure mercury lamp under 8 bar of H$_2$. Labelled signals are attributable to 4 (triangle), 2 (star), 6 (circle), respectively.
Figure S6. $^1$H NMR spectrum of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure mercury lamp under 8 bar of D$_2$. Labelled signals are attributable to 2 (star) and 6 (circle), respectively. The presence of the NCH and simultaneous absence of the hydride resonances of 2 and 6 proves the incorporation of D$_2$ from the gas phase.

Figure S7. $^1$H NMR spectrum of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure mercury lamp under 8 bar of a mixture of dihydrogen isotopomers. Labelled signals are attributable to 2 (star) and 6 (circle), respectively.
Figure S8. Hydride region of the $^1$H NMR spectrum of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure Hg-lamp under 8 bar of a mixture of dihydrogen isotopomers (blue trace) and simulation (red trace) as a superposition of signals attributable to 6 and 6-D$_1$ (ratio 0.56:1) with $J_{HP} = 31.8$ Hz and $J_{HD} = 5.5$ Hz. The increased linewidth of the signal of 6 ($\Delta \nu_{1/2} = 18.6$ vs. 4.8 Hz) reflects an additional relaxation contribution arising from dipolar coupling between the two $^1$H nuclear spins in 6, which is absent in the D$_1$-isotopomer.

Figure S9. $^1$H, $^{31}$P-HMQC NMR spectrum and expansion of a solution of 4 in THF-D$_8$ after 7.5 h of irradiation with a medium pressure mercury lamp under 8 bar of a mixture of hydrogen isotopomers. Spectral labels indicate cross-peaks attributable to different isotopomers of 2.
Kinetic study of the photolysis of 2 and 4 under H₂-pressure

A solution of 2 or 4 (7 mg, 7 μmol) in THF-D₂ (0.5 mL) was transferred to a medium-walled high pressure NMR tube and degassed by completing three freeze-pump-thaw cycles. The NMR tube was pressurized with H₂, followed by acquisition of an initial ¹H NMR spectrum. The solution was then irradiated for different intervals with a medium-pressure mercury lamp (up to a total irradiation time of 270 min), and a ¹H NMR spectrum recorded after each interval. Evaluation of the product distribution at each point in time was performed by spectral integration of suitable signals using the residual signal of the deuterated solvent as reference. Results obtained under different H₂-presures are summarized in Tables S1 to S4. Evaluation of the data revealed that the consumption of starting material 2 during the initial reaction stages follows a pseudo-first-order rate law. The rate constants decrease with increasing H₂-pressure without that a quantitative relation becomes apparent (Figure S10). Further evaluation of the data was hampered, among others, by the appearance of an unidentified product arising most likely from decomposition.

Table S1. Product distribution over time during photolysis of 2 under 1 bar of Argon.

| Irradn. [min] | 2 [a] | 4 [a] | 6 [a] | unidentified [a] |
|---------------|-------|-------|-------|------------------|
| 0             | 100   | 0     | 0     | 0                |
| 7             | 94.8  | 5.2   | 0     | 0                |
| 17            | 81.9  | 13.4  | 1.4   | 4.7              |
| 50            | 46.5  | 32.8  | 0     | 20.8             |
| 120           | 17.3  | 53.2  | 0     | 29.5             |
| 180           | 6.9   | 62.0  | 2.9   | 28.2             |
| 270           | 0     | 70.7  | 4.4   | 24.9             |

[a] normalized in % of the total integral.

Table S2. Product distribution over time during photolysis of 2 under 3 bar of H₂.

| Irradn. [min] | 2 [a] | 4 [a] | 6 [a] | unidentified [a] |
|---------------|-------|-------|-------|------------------|
| 0             | 100   | 0     | 0     | 0                |
| 7             | 94.0  | 2     | 4     | 0                |
| 17            | 87.6  | 4.5   | 7.9   | 0                |
| 50            | 60.8  | 11.9  | 16.0  | 11.3             |
| 120           | 26.1  | 31.6  | 12.8  | 29.5             |
| 180           | 17.8  | 42.9  | 11.0  | 28.3             |
| 270           | 12.1  | 50.4  | 10.2  | 27.3             |

[a] normalized in % of the total integral.

Table S3. Product distribution over time during photolysis of 2 under 8 bar of H₂.

| Irradn. [min] | 2 [a] | 4 [a] | 6 [a] | unidentified [a] |
|---------------|-------|-------|-------|------------------|
| 0             | 100   | 0     | 0     | 0                |
| 7             | 92.6  | 2.7   | 4.7   | 0                |
| 17            | 86.6  | 4.3   | 9.0   | 0                |
| 50            | 65.3  | 14.8  | 20.0  | 5.3              |
| 120           | 34.1  | 33.9  | 24.9  | 7.1              |
| 180           | 21.4  | 42.1  | 24.9  | 10.6             |
| 270           | 16.4  | 49.9  | 23.7  | 10.1             |

[a] normalized in % of the total integral.
Table S4. Product distribution over time during photolysis of 4 under 8 bar of H₂.

| Irradn. [min] | 4 [a] | 2 [a] | 6 [a] |
|--------------|-------|-------|-------|
| 0            | 100   | 0     | 0     |
| 7            | 97.5  | 0     | 2.5   |
| 17           | 94.2  | 0     | 5.8   |
| 50           | 84.9  | 4.2   | 10.9  |
| 120          | 73.9  | 10.6  | 15.5  |
| 180          | 70.5  | 12.8  | 16.7  |
| 270          | 66.8  | 13.6  | 19.6  |

[a] normalized in % of the total integral.

Figure S10: Plot of ln([2]) vs. t showing the time evolution of the concentration of 2 during the initial stages of photolysis experiments under Ar, 3 bar of H₂, and 8 bar of H₂ initial pressure. The straight lines represent the results of linear fits to the data.

Reaction of 6 with D₂

A solution of 6-H₂ was generated photochemically from 4 and H₂ (8 bar) in a high pressure NMR tube as described above. The solution was then frozen in liq. N₂ and the NMR tube evacuated to remove gaseous H₂ and, after the solution had been allowed to warm up to ambient temperature, pressurized with D₂ (8 bar). The sample was agitated to ensure dissolution of D₂ in the liquid phase. A 1H NMR spectrum run immediately afterwards showed that the NCH signals of 2 and 6 as well as the hydride signal of 2 were still visible whereas the hydride signal of 6 had disappeared, pointing out that 6 had undergone rapid H₂/D₂-exchange whereas 2 was obviously inert (Figure S11).

Figure S11. 1H NMR spectra of a solution of 4 in THF-D₈ subjected to photolysis under 8 atm of H₂ (blue trace) and after exposure with 8 atm of D₂ (red trace). The labelled NCH and hydride resonances are attributable to 2 (star), 4 (triangle), and 6 (circle).
Thermal conversion of 6 under H₂ atmosphere

Photolysis of 4 under H₂ (8 bar) in a high pressure NMR tube was carried out as described above. A ¹H NMR spectrum was recorded and the sample then kept at 40 °C for 336 h without further irradiation, with small interruptions in regular intervals to acquire NMR spectra for monitoring the progress of the reaction. Analysis of the composition of the mixture at each point in time was performed by evaluating the integrals of the signals of NCH-units, using the resonance of the deuterated solvent as internal reference. The results (Table S5, Figure S12) confirm that eventual conversion of 6 to form 2 and, to a minor extent, 4, took place.

Table S5. Evolution of product distribution in a solution containing a mixture of 2/4/6 at 40 °C under 8 bar of H₂.

| time [h] | 4 [a] | 2 [a] | 6 [a] |
|----------|-------|-------|-------|
| 0        | 70.2  | 11.3  | 18.6  |
| 0.5      | 70.4  | 12.2  | 17.4  |
| 1.5      | 70.4  | 14.3  | 15.3  |
| 3.5      | 71.0  | 15.7  | 12.3  |
| 10.5     | 71.8  | 21.4  | 6.3   |
| 30.5     | 72.9  | 23.6  | 3.5   |
| 103.5    | 73.1  | 24.7  | 2.2   |

[a] normalized in % of the total integral.

Figure S12. Expansion of ¹H NMR spectra of a solution of 4 in THF-D₈ under 8 bar of H₂ recorded after 2 h of photolysis (blue trace) and subsequent heating to 40 °C (without further irradiation) for 3.5 h (red trace), 10.5 h (green trace and 336 h (purple trace). Labelled signals are attributable to 2 (triangle), 4 (star), and 6 (circle), respectively.
Thermal conversion of 6 under vacuum

A solution containing 6 was generated photochemically from 4 and H₂ (8 bar) in a high pressure NMR tube as described above. A ¹H NMR spectrum was recorded and the sample then frozen in liq. N₂. The NMR tube was evacuated and then allowed to warm to ambient temperature, heated to 40 °C under autogenous pressure of the solvent, and kept at this temperature for 516 h without further irradiation with small interruptions to acquire NMR spectra for monitoring the progress of the reaction. The composition of the mixture was analyzed at each point in time by evaluating the integrals of the signals of NCH-units, using the resonance of the deuterated solvent as internal reference. The results (Table S6, Figure S13) confirm the eventual conversion 6 → 4.

Table S6. Evolution of product distribution in a solution containing a mixture of 2/4/6 at 40 °C in the absence of gaseous H₂.

| Reaction time [h] | 4 [%] | 2 [%] | 6 [%] |
|-------------------|-------|-------|-------|
| 0                 | 72.9  | 11.4  | 15.7  |
| 1.5               | 74.1  | 11.4  | 14.6  |
| 18                | 75.6  | 12.2  | 12.2  |
| 66                | 77.5  | 12.8  | 9.7   |
| 200               | 81.0  | 12.7  | 6.3   |
| 372               | 84.2  | 12.8  | 3.0   |
| 516               | 86.3  | 12.0  | 1.7   |

[a] normalized in % of the total integral.

Figure S13. Expansion of ¹H NMR spectra of a solution of 4 in THF-D₈ recorded after 2 h of photolysis under 8 bar of H₂ and removal of gaseous H₂ (blue trace) and subsequent heating to 40 °C (without further irradiation) for 90 h (red trace), 272 h (green trace and 516 h (purple trace). Labelled signals are attributable to 2 (triangle), 4 (star), and 6 (circle), respectively.

Hydrogenation of Styrene

(a) Styrene (1.5 μL, 1.4 mg, 13 μmol) was added to a solution of 4 (2 mg, 2 μmol, 16 mol-% based on styrene) in THF-D₈ (0.5 mL). The sample was transferred to a medium-walled high pressure NMR tube and degassed by completing with three freeze-pump-thaw cycles. The NMR tube was then pressurized with H₂ (8 bar initial pressure). After acquisition of a reference ¹H NMR spectrum, the solution was irradiated for 11.5 h with a medium pressure Hg lamp, with short interruptions to acquire ¹H NMR spectra for reaction monitoring. Analysis of the composition of the mixture at each point in time was performed by evaluating the integrals of the signals of NCH-units and the CH₂-signal of ethylbenzene, using a silicone resonance as internal reference (see Table S7). Near quantitative conversion of styrene to ethylbenzene (95% based on the original amount of styrene) occurred within 11.5 h of irradiation time (Figure S14). Analysis of the phosphorus-containing species at the end of the reaction revealed the presence of 4 (45% based on the amount originally present), 6 (10%), secondary diazaphospholene 1 (24%) and a species X (21%) tentatively identified as P-phenethyl-substituted diazaphospholene arising from phosphinilation of styrene by 1 (Table S7, Figure S15, S18).

(b) Hydrogenation of styrene (3 μL, 2.7 mg, 26 μmol) in THF-D₈ (0.5 mL) in the presence of 4 (1 mg, 1 μmol, 4 mol-% based on styrene) was carried out as described above to result in 71% conversion (Figure S16). Analysis of the phosphorus-containing species at the end of the reaction indicated that only minor amounts of phosphinonium complexes (8% of 4 and traces of 6) were
still present and that extensive deactivation to give 1 (30%) and 4 (62%) was observable (Table S8, Figure S17).

(c) To try identifying the catalytically active species in the hydrogenation, a sample containing styrene and 4 (16 mol-%) under H2 (8 bar) was prepared as described above and irradiated for 20 min with a medium-pressure Hg lamp. An NMR-spectroscopic analysis confirmed that a significant amount of 6 (7%) and a small amount of ethylbenzene (16%; both values based on the amount of 4 initially present, see Figure S19) had formed. The solution was then stored at 20 °C for 18 h without further irradiation. Subsequent NMR spectroscopic analysis revealed that 4 had been completely consumed while the amount of ethylbenzene had increased (Figure S19). Signals of 1 and X were not detectable, suggesting negligible decay of the NHP complex during the rather short photolysis time. Quantitative evaluation of the changes in signal integrals allowed us to calculate a turnover number TON = Δn(ethylbenzene)/Δn(ethylene) = 9.6 which suggests that the dihydrogen complex transfers H2 to the substrate in a thermal reaction and can perform several turnovers without additional photochemical activation.

(d) Control experiments were carried out using the same procedure as described above. Employing Cr(CO)3(naphthalene) (2 mg, 7.6 µmol, 16 mol-% based on styrene) as pre-catalyst resulted in 18 % conversion of styrene to ethylbenzene after 17 h of irradiation (Figure S20), implying an essentially stoichiometric reaction. No formation of ethylbenzene was observed in the presence of 1 (2 mg, 4.9 µmol, 16 mol-% based on styrene, Figure S21) or in the absence of any catalyst (Figure S22).

Table S7. Reaction monitoring of the photohydrogenation of styrene (16 mol-% 4, 8 bar H2 initial pressure)

| Reaction time [h] | 4 [%] | 6 [%] | 1 [%] | X [%] | Ethylbenzene [%] |
|------------------|-------|-------|-------|-------|-----------------|
| 0                | 100   | 0     | 0     | 0     | 0               |
| 2.00             | 66.6  | 13.5  | 6     | 13.9  | 171             |
| 3.33             | 54.8  | 15.7  | 10.8  | 18.7  | 345             |
| 4.33             | 51.3  | 14.9  | 13.5  | 20.3  | 412             |
| 6.00             | 47.7  | 15.6  | 15.5  | 21.1  | 495             |
| 7.00             | 47.9  | 13.4  | 18.2  | 20.4  | 542             |
| 8.00             | 44.3  | 13.6  | 19.0  | 23.4  | 578             |
| 9.75             | 43.0  | 13.4  | 21.9  | 21.8  | 602             |
| 11.5             | 44.6  | 9.7   | 24.2  | 21.5  | 617             |

[a] normalized to n(4),o = 100 %.

Figure S14. Expansion of the 1H NMR spectrum of a solution of styrene and 4 (16 mol-%) in THF-D8 under 8 bar of H2 before (blue trace) and after (red trace) 11.5 h of irradiations. Integrals refer to a CH signal of styrene and the CH2 group of ethyl benzene relative to a silicone standard.

Figure S15. Kinetic plot showing the time evolution of ethylbenzene (left) and phosphorus-containing species (right) during photohydrogenation of styrene in the presence of 16 mol-% 4 [TON = n(Ethylbenzene)/n(4),o].
Table S8. Reaction monitoring of the photohydrogenation of styrene (4 mol-% 4, 8 bar H₂ initial pressure).

| Reaction time [h] | 4 [%] | 6 [%] | 1 [%] | X [%] | Ethylbenzene [%] |
|-------------------|-------|-------|-------|-------|------------------|
| 0                 | 100   | 0     | 0     | 0     | 0                |
| 2.00              | 40.1  | 5.7   | 28.6  | 25.6  | 747              |
| 3.00              | 34.1  | 4.0   | 28.7  | 33.2  | 971              |
| 5.00              | 22.0  | 1.7   | 31.4  | 44.9  | 1440             |
| 60                | 15.6  | 1.5   | 31.3  | 51.6  | 1530             |
| 7.00              | 11.0  | 1.1   | 30.6  | 56.7  | 1570             |
| 8.75              | 10.2  | 0.9   | 29.8  | 57.7  | 1670             |
| 10.50             | 8.5   | 0.4   | 29.6  | 61.5  | 1770             |

[a] normalized to n(4)ₜ₀ = 100 %.

Figure S16. Expansion of the ¹H NMR spectrum of a solution of styrene and 4 (4 mol-%) in THF-D₈ under 8 bar of H₂ before (blue trace) and after (red trace) 10.5 h of irradiations. Integrals refer to a CH signal of styrene and the CH₂ group of ethyl benzene relative to a silicone standard.

Figure S17. Kinetic plot showing the time evolution of ethylbenzene (left) and phosphorus-containing species (right) during photohydrogenation of styrene in the presence of 4 mol-% of 4 (TON = n(Ethylbenzene)/n(4)ₜ₀).
Figure S18. Expansion of the $^1$H,$^{31}$P HMQC NMR spectrum at the end of the photo-hydrogenation of styrene in the presence of 4 mol-% of 4 showing the correlations connected with the $^{31}$P NMR signal at 117 ppm attributable to X. The correlations result from spin coupling of the $^{31}$P nucleus with protons of an NCH unit ($^1$H 5.8 ppm) and a PhCH$_2$-unit ($^1$H 2.4 ppm) and lead us to tentatively assign the molecular structure of X as a diazaphospholene bearing a P-CH$_2$CH$_2$Ph substituent.

Figure S19. Expansion of the $^1$H NMR spectrum of a solution of 4 and styrene in THF-D$_8$ after 20 min of irradiation under 8 bar of H$_2$ (red trace) and after storage of the solution for 18 h at 20 °C (blue trace). Labelled signals are attributable to styrene (S), ethylbenzene (E), 4 (triangle), and 6 (circle), respectively.

Figure S20. $^1$H NMR spectra of a solution of styrene and [Cr(CO)$_3$(naphthalene)] in THF-D$_8$ under 8 atm of H$_2$ before irradiation (blue trace) and after 17h of irradiation with a medium pressure Hg lamp [red trace]. Labelled signals are attributable to styrene (S), ethylbenzene (E), [Cr(CO)$_3$(naphthalene)] (circle) and naphthalene (N).
**Figure S21.** $^1$H NMR spectra of a solution of styrene and 1 n THF-D$_8$ under 8 atm of H$_2$ before (blue trace) and after 17h of irradiation with a medium pressure Hg lamp (red trace). Labelled signals are attributable to styrene (S) and 1 (circle).

**Figure S22.** $^1$H NMR spectra of a solution of styrene in THF-D$_8$ under 8 atm of H$_2$ before (blue trace) and after 17 h of irradiation with a medium pressure Hg lamp (red trace). Labelled signals are attributable to styrene (S) and an unidentified by-product (U).
NMR Spectra

Figure S23. $^1$H NMR spectrum of 2 in C$_6$D$_6$ with expanded regions displaying the PH and CrH signals.

Figure S24. Expansion of the $^1$H-EXSY NMR spectrum of 2 in C$_6$D$_6$ showing the exchange cross-peak between PH and CrH signals.
Figure S25. $^{31}\text{P}^\{1\text{H}\}$ NMR spectrum of 2 in C$_6$D$_6$ (bottom trace). Framed inserts display expansions of the two signals in the $^{31}\text{P}^\{1\text{H}\}$ (top row) and $^{31}\text{P}$ (bottom row) NMR spectrum.

Figure S26. $^{1}\text{H},^{31}\text{P}$ HMQC NMR spectrum of 2 in C$_6$D$_6$. 
Figure S27. $^{13}$C($^1$H) NMR spectrum of 2 in C$_6$D$_6$.

Figure S28. $^1$H NMR spectrum of 4 in C$_6$D$_6$.

Figure S29. $^{31}$P($^1$H) NMR spectrum of 4 in C$_6$D$_6$. 
Figure S30. $^{13}$C($^1$H) NMR spectrum of (2) in C$_6$D$_6$.

Figure S31. $^1$H NMR spectrum of 5[BAr$_4^+$] in C$_6$D$_6$/THF-D$_8$ 5:1 with expansions showing the regions of the CrH and NCH signals.

Figure S32. $^{31}$P($^1$H) NMR spectrum of 5[BAr$_4^+$] and expanded region of the $^{31}$P NMR spectrum (insert) in C$_6$D$_6$/THF-D$_8$ 5:1.
Figure S33. $^{13}$C{H} NMR spectrum of 5[BArF$_4$] in C$_6$D$_6$/THF-D$_8$ 5:1.

Figure S34. $^{11}$B{H} NMR spectrum of 5[BArF$_4$] in C$_6$D$_6$/THF-D$_8$ 5:1.

Figure S35. $^{31}$P{H} (top) and $^{31}$P NMR Spectrum of a solution of 2 in C$_6$D$_6$/CD$_3$CN (1:6) showing signals attributable to 2 (triangles) and 3b (star).
Figure S36. $T_1$ relaxation times for the hydride signals of 2 and 6 determined by the inversion-recovery method at different temperatures. Minimum values (at 253 K): $T_{1,\text{min}} = 18$ ms (6), 739 ms (2).

Figure S37. $^1$H NMR Spectrum of a solution of 2 in C$_6$D$_6$/CD$_3$CN (1:6) showing signals attributable to 2 (triangles) and 3b (star). The inserts display expansions of the regions containing the PH and NCH signals.
Figure S38. $^1$H,$^3$P HMQC NMR spectrum of a solution of 2 in C$_6$D$_6$/CD$_3$CN (1:6).
High Resolution Mass Spectra

Figure S39. (+)-ESI-HRMS of 2 (top left), 4 (top right) and 5[Bar4] (bottom left) and (-)-ESI-HRMS of 5[Bar4] (bottom right). The top trace in each quadrant displays the observed spectrum and the bottom trace the simulated isotope pattern.

UV-VIS-Spectra

Figure S40: UV-VIS spectrum of 4 (0.02 mM in THF).
Crystallographic Studies

X-ray diffraction data were collected on a Bruker diffractometer equipped with a Kappa Apex II Duo CCD-detector and a KRYO-FLEX cooling device with Mo-Kα radiation (λ = 0.71073 Å) at 130(2) K for 2/3b (co-crystal containing both molecules in 1:1 ratio) and with Cu-Kα radiation (λ = 1.5406 Å) at 135(2) K for 5[BArf4]. The structures were solved with direct methods (SHELXS-97) and refined with a full-matrix least squares scheme on F2 (SHELXL-2014 and SHELXL-97). Semi-empirical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogens atoms using a riding model. The three carbonyl and one hydride ligands in 2 are disordered on four positions around the chromium atoms. Refinement under application of SIMU and SUMP with free occupation on all four positions at Cr gave three CO ligands displaced on four positions. The position of the hydrogen atom on the metal could not be refined. However, the presence of significantly different P-Cr distances, different coordination environments on the phosphorus atoms and a freely refined hydrogen atom on the pyramidal phosphorus atom, as well as conclusive NMR data provide proof for a phosphonium phosphane hydride complex with a metal bound hydrogen atom. In general, the data of the 2/3b co-crystal are very weak (Rint = 27.9 %). In the crystal of 5[BArf4], the fluorine atoms on three CF3 substituents in the anion displayed large anisotropic displacement parameters, and a refinement of disorder was performed by using split positions for each atom and refining the occupation of both positions with isotropic displacement parameters. The occupancies gained were then fixed and used for the anisotropic refinement of the disordered CF3 groups. SADI was applied for C-F, F-F and 1.3-C-F distances. RIGU was applied for the displacement parameters, and ISOR for the disordered F atoms. CCDC-2005812 (2/3b) and CCDC-2005814 (5[BArf4]) contain the crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

| Table 59. Crystallographic data of 2/3b and 5[BArf4] |
|------------------------------------------------------|
| **Empirical formula**                                |
| 2/3b                                                 |
| C12H125CrN5O2P4                                      |
| 5[BArf4]                                             |
| C18H26B7CrF18N6O2P2                                  |
| **Formula weight (g·mol⁻¹)**                         |
| 1947.29                                             |
| 1815.33                                             |
| **T (K)**                                            |
| 130(2)                                              |
| 135(2)                                              |
| **a [Å]**                                           |
| 25.6854(10)                                         |
| 12.5935(3)                                         |
| **b [Å]**                                           |
| 20.8290(9)                                         |
| 16.7577(4)                                         |
| **c [Å]**                                           |
| 40.6993(18)                                        |
| 21.3290(5)                                         |
| **α (°)**                                           |
| 90                                                  |
| 95.4141(1)                                         |
| **β (°)**                                           |
| 90                                                  |
| 99.5511(1)                                         |
| **γ (°)**                                           |
| 90                                                  |
| 92.236(1)                                          |
| **V [Å³]**                                          |
| 21774.2(16)                                        |
| 4412.18(18)                                        |
| **Crystal system**                                  |
| Orthorhombic                                        |
| Triclinic                                           |
| **Space group**                                     |
| PbcA                                                |
| P-1                                                 |
| **Z**                                               |
| 8                                                   |
| 2                                                   |
| **ρcalc [g·cm⁻³]**                                  |
| 1.188                                               |
| 1.366                                               |
| **µ [mm⁻¹]**                                        |
| 0.314                                               |
| 2.291                                               |
| **Crystal dimensions [mm]**                         |
| 0.122 x 0.121 x 0.081                               |
| 0.167 x 0.127 x 0.097                               |
| **f(000)**                                          |
| 8336                                                |
| 1868                                               |
| **Rint**                                            |
| 0.2791                                              |
| 0.0456                                              |
| **Observed reflections [>2σ(I)]**                   |
| 170081                                              |
| 65546                                              |
| **No of unique reflections**                        |
| 19979                                              |
| 15033                                              |
| **Restraints**                                      |
| 13                                                 |
| 1584                                               |
| **Parameters**                                      |
| 1190                                               |
| 1087                                               |
| **R1 [>2σ(I)]**                                     |
| 0.0827                                             |
| 0.0434                                             |
| **wR2 (all data)**                                  |
| 0.2301                                             |
| 0.1126                                             |
| **Goodness-of-fit on F²**                           |
| 0.979                                              |
| 1.023                                              |
| **Largest diff. peak and hole [e·Å⁻³]**             |
| 0.776 and -0.411                                   |
| 0.456 and -0.390                                   |

Computational Studies

**General remarks.** All computations were performed with the Gaussian 16 program package.8 DFT calculations were carried out using the ωB97xD8 functional that had previously been successfully applied for the study of hydrogenation of NHP complexes,10 using an ultrafine grid for numerical integration and Weigend’s and Ahirich’s def2-tzvp basis sets.11 The molecular structures were established by full energy optimization. Subsequent stability tests (keyword stable=opt) confirmed that the electronic states are not compromised by singlet/triplet or RHF/UBF instabilities. Harmonic vibrational frequency calculations were finally carried out at the same level to establish the nature of the stationary points obtained as local minima (only positive normal modes) or transition states (one imaginary normal mode), and to calculate standard Gibbs free energies ΔG0 (referring to p=1 bar and T=298K). NBO population analyses were carried out using the NBO module implemented in the Gaussian package. The electronic spectrum of 4th was computed at the TD-ωB97xD/def2-tzvp level of theory. The relaxed molecular structure of the excited state was located by energy optimization of the first excited state identified in the TD-DFT calculation at the ωB97xD/def2-svp level of theory, and its energy recalculated at the final geometry at the ωB97xD/def2-tzvp level.
Table S10. Computed energies (in Hartree/particle) and atomic coordinates (in Å) for data of $2^{44}$He, $4^{44}$He, $4^{44}$He, $6^{44}$He, TS1, TS2

| Complex 2$^{44}$ | Charge = 0, Multiplicity = 1 | E(Ru(897xD)) = -2601.94905120 |
|---|---|---|
| Zero-point correction = 0.293902 (Hartree/Particle) | Thermal correction to Energy = 0.318439 | Thermal correction to Enthalpy = 0.319383 |
| Thermal correction to Gibbs Free Energy = 0.235454 | | |
| C | 0.0891497577 | 1.6866654266 | 1.1773628587 |
| Cr | 0.0431447163 | 0.090245362 | 0.325289913 |
| P | 2.0907755914 | 0.0082433273 | -0.158657054 |
| N | 3.3245120109 | -1.121705234 | 0.1529611342 |
| C | 4.5432656297 | -0.6291946085 | -0.484196052 |
| C | 4.4579266815 | 0.6706667439 | -0.7618400377 |
| C | 3.2053579448 | 2.5221958431 | -0.88074159 |
| O | 0.1171334566 | 2.7136248227 | 1.6832682693 |
| P | -0.2081465165 | 0.4546040937 | -0.100492711 |
| N | -3.4462137915 | -0.0928539113 | 0.6709322576 |
| C | -4.5417952972 | -0.1537191119 | -0.204994584 |
| C | -4.6152514922 | -0.161207612 | -1.482389335 |
| C | -2.7729737262 | -0.10446613 | -1.640935517 |
| C | -2.2062297843 | 0.1902066366 | -2.953727886 |
| O | -0.15636648 | -1.613774011 | -0.594322765 |
| O | -0.2601969623 | -2.613654829 | -1.1482785378 |
| C | -0.1178451531 | -0.898763512 | 1.9385366323 |
| O | -0.2276836939 | -1.4661903709 | 2.9318792204 |
| C | 3.1547419399 | -2.498150197 | 0.4059754553 |
| C | -3.6268988974 | 0.276003997 | 0.2054796256 |
| H | 5.4093259787 | -1.268010968 | -0.4981166462 |
| H | 5.2408725065 | 1.3189015211 | -1.118660746 |
| H | -5.5418168696 | -0.268734802 | 0.1850004323 |
| H | -4.8012229903 | -0.291235091 | -2.3452800802 |
| H | -2.3275190912 | -1.240656922 | -3.219690423 |
| H | -1.1434913033 | -0.044197423 | -2.931224028 |
| H | -2.6296631611 | -0.418675446 | -3.688260176 |
| H | -4.4414490366 | -0.3337142148 | -2.9029429486 |
| H | -2.7052363917 | 0.085212432 | 2.6054550678 |
| H | -3.8928606573 | 1.334552595 | 1.707705052 |
| H | 3.2612962886 | 2.8276418238 | -1.8218331534 |
| H | 1.7208745187 | 2.5784137077 | -0.9829181641 |
| H | 3.1231219038 | 3.198924582 | -0.085803991 |
| H | 3.9096895587 | -2.7677597102 | 1.1358372026 |
| H | 2.1665161097 | -2.600442862 | 0.8704114547 |
| H | -2.3671868678 | 1.867985669 | -0.2610182249 |
| H | -0.122471534 | 0.870938313 | -1.0773718222 |

| Complex 4$^{44}$ | Charge = 0, Multiplicity = 1 | E(Ru(897xD)) = -2600.79353045 |
|---|---|---|
| Zero-point correction = 0.277936 (Hartree/Particle) | Thermal correction to Energy = 0.302495 | Thermal correction to Enthalpy = 0.303439 |
| Thermal correction to Gibbs Free Energy = 0.221393 | | |
| C | -0.1758589569 | 1.8608185516 | 0.8560332016 |
| Cr | 0.0000053169 | -0.0000098121 | 0.769668554 |
| P | 1.8324113505 | 0.1780072904 | -0.1911621389 |
| N | 3.2548890604 | -0.7199360564 | -0.2623348704 |
| C | 4.2176647274 | -0.1879839482 | -0.1048193214 |

| Complex 4$^{44}$ ($1^{1}$ excited state, optimized) | Charge = 0, Multiplicity = 1 | E(Ru(897xD)) = -2600.7124853 |
|---|---|---|
| Zero-point correction = 0.277385 (Hartree/Particle) | Thermal correction to Energy = 0.302223 | Thermal correction to Enthalpy = 0.303167 |
| Thermal correction to Gibbs Free Energy = 0.219695 | | |
| C | 0.3918423264 | 1.0628632522 | 0.3086714733 |
| Cr | 0.1175338914 | -0.6169148333 | -0.436485327 |
| P | 2.456511175 | -0.595986516 | -0.6536975929 |
| N | 3.3475409232 | 0.0719855765 | 0.6674917347 |
| C | 4.0271446742 | 1.2236397534 | 0.3416989439 |
| TS 2       | TS 1       |
|-----------|-----------|
| Charge     | Charge     |
| 0          | 0         |
| Multiplicity | 1         |
| Multiplicity | 1         |
| E(Ru897xD) | E(Ru897xD) |
| = 2601.892603 | = 2601.8971958 |
| Zero-point correction | Zero-point correction |
| = 0.288136 (Hartree/Particle) | = 0.289114 (Hartree/Particle) |
| Thermal correction to Energy | Thermal correction to Energy |
| = 0.313627 | = 0.315668 |
| Thermal correction to Enthalpy | Thermal correction to Enthalpy |
| = 0.314571 | = 0.316612 |
| Thermal correction to Gibbs Free Energy | Thermal correction to Gibbs Free Energy |
| = 0.230205 | = 0.231190 |
| C       | C         |
| 0.0308787426 | 0.4096173619 |
| 1.650327852 | 1.1187311003 |
| 0.9303843371 | 0.7381072281 |
| Cr       | C         |
| 0.075908225 | 0.593331648 |
| 0.2395898728 | 1.9051879458 |
| -0.304634551 | 1.5504696898 |
| P       | Cr         |
| 0.234339541 | 0.116513982 |
| 0.116513982 | 0.197823872 |
| -0.197823872 | -0.251489171 |
| N       | C         |
| 0.2547903276 | 0.1191058449 |
| -1.1501130675 | -1.405326358 |
| 0.0102965594 | 0.8486232912 |
| C       | C         |
| 0.4558290309 | -0.379906518 |
| -0.7541918145 | -1.1605867887 |
| 0.1158467107 | -1.3361536826 |
| C       | C         |
| 0.4654979327 | -0.4979897212 |
| 0.5790692059 | -0.1998238728 |
| 0.8007952567 | -0.251489171 |
| N       | C         |
| 0.3422731762 | 0.2805973577 |
| 1.1856998327 | 0.1984986325 |
| 0.0302948482 | 0.1675521513 |
| C       | C         |
| 0.2525328525 | 0.2922516699 |
| 3.2667677065 | -0.1524508838 |
| 0.0481943872 | -0.5089507097 |
| N       | C         |
| 0.0379667151 | -0.1946747584 |
| 2.5157798124 | -0.0030793652 |
| 1.683780772 | -0.6828039337 |
| P       | C         |
| -0.2237799067 | 0.3716031653 |
| 0.6359243245 | -0.7241251662 |
| -0.6522958952 | -0.1846208291 |
| N       | C         |
| -0.3577418599 | 0.2966163699 |
| 0.596473019 | -1.3470092676 |
| 0.6268063111 | -2.87508214 |
| C       | C         |
| -0.4370906439 | 0.1354165835 |
| -0.3433630355 | -1.7063894871 |
| 0.3621468354 | -1.71945908 |
| C       | C         |
| -0.4259725976 | 0.1507825301 |
| -0.8894648565 | -2.6388464272 |
| -0.8486659825 | -2.388610879 |
| N       | C         |
| -0.3176074034 | -0.4691060581 |
| 0.1507825301 | 0.1491661567 |
| 0.689546696 | 0.689546696 |
| C       | C         |
| -0.3270620836 | -0.30414124 |
| -0.30414124 | -0.30414124 |
| -0.3270620836 | -0.30414124 |
| C       | C         |
| -0.0873174012 | 0.3656120595 |
| -1.04254383194 | -0.0920705683 |
| 1.6765210609 | 2.1083561302 |
| N       | C         |
| -0.1889013522 | 0.2930478247 |
| -1.8460738244 | 1.4214127133 |
| -2.245550777 | -1.857468417 |
| C       | C         |
| -0.1885852914 | 0.3994121024 |
| -1.0633043484 | 0.4199490295 |
| 0.97747539 | 0.4714000636 |
| O       | O         |
| -0.395003492 | -2.7678172088 |
| -1.8690244993 | 1.0855023238 |
| 0.7464040476 | 1.7161343464 |

[a] at the Ru897xD/def2-tzvp/Ru897xD/def2-svp level. [b] at the Ru897xD/def2-svp level.
| Charge | Multiplicity | E(Ru897xD) = 3367.73710269 | Charge | Multiplicity | E(Ru897xD) = 3368.92988211 |
|--------|-------------|----------------------------|--------|-------------|----------------------------|
| C 16.77045110431 | 7.0582903654 | 12.8946427834 C | -5.905728 | 1.136123 | -0.761136 |
| O 15.6913371439 | 6.8323218738 | 12.5629079194 C | -5.065475 | 0.465898 | 0.126091 |
| Cr 18.5119812944 | 7.2686392704 | 13.54350267 C | -3.810488 | 0.982556 | 0.435751 |
| Cr 18.3003225631 | 5.4981526626 | 14.045912669 C | -3.39458 | 2.174845 | -0.159197 |
| Cr 18.1685942697 | 4.3981000997 | 14.3581728834 C | -4.226637 | 2.843697 | -1.057527 |
| P 17.9329528923 | 8.8430920588 | 14.7659578677 C | -5.485249 | 2.327826 | -1.350757 |
| N 16.6460483994 | 9.7939033338 | 13.6746811539 N | -2.111877 | 2.71925 | 0.154202 |
| N 15.6320602458 | 9.9212043071 | 13.674434796 C | -1.959231 | 3.991483 | 0.702381 |
| P 19.3438855424 | 7.8096602027 | 11.7199532274 C | -0.666539 | 4.268588 | 0.961524 |
| N 20.8498455693 | 8.5124515947 | 11.2935016177 N | 0.165683 | 3.217533 | 0.58991 |
| C 21.88763776 | 8.7649887986 | 12.2347752919 C | 1.568404 | 3.200416 | 0.857208 |
| C 20.2023799638 | 7.050525999 | 14.3137214826 C | 2.473578 | 2.960403 | -0.177129 |
| C 21.224454478 | 6.7998027712 | 14.7805118691 C | 3.831196 | 2.846632 | 0.110103 |
| N 18.5287314792 | 9.7382626607 | 16.1114404076 C | 4.288846 | 3.003839 | 1.416842 |
| C 19.7018814907 | 9.4163379391 | 16.841488223 C | 3.383498 | 3.274831 | 2.442149 |
| C 17.7576942477 | 10.8578232575 | 16.4370413732 C | 2.021322 | 3.361023 | 2.168263 |
| C 16.6882018145 | 10.980325262 | 15.6320412949 H | 2.116673 | 2.840222 | -1.200366 |
| N 18.8753948384 | 9.8121103328 | 10.0719559342 H | 1.300588 | 3.521287 | 2.972875 |
| C 17.6178256508 | 9.5392079025 | 9.5430897877 H | -1.348785 | 0.450625 | 1.116519 |
| C 19.85017825 | 8.5699908849 | 9.267004998 H | -3.878106 | 3.766525 | -1.531412 |
| C 20.9689881427 | 8.8556150728 | 9.9502321906 P | -0.655311 | 1.876534 | -0.05948 |
| H 18.0317344502 | 11.4827450718 | 17.2832207262 Cr | -0.05618 | -0.02685 | -0.64176 |
| C 15.9120712859 | 11.7417193094 | 15.6601606595 P | 0.465171 | -2.223056 | -0.85525 |
| H 19.667812331 | 8.7078857785 | 8.199841775 N | -0.2463 | -3.408062 | 0.192536 |
| C 21.8931151567 | 9.3011248046 | 9.579492507 C | -1.541994 | -3.334401 | 0.732772 |
| C 20.638897178 | 10.4159904168 | 17.1262476282 C | -1.756695 | -3.511689 | 2.10509 |
| C 21.7823255192 | 10.1103435135 | 17.8597588718 C | -3.046745 | -3.448947 | 2.626554 |
| C 22.0102297563 | 8.80517808 | 18.2937202748 C | -4.135329 | -3.192039 | 1.793029 |
| C 21.0760261438 | 7.8113744006 | 18.0073193646 C | -3.921686 | -3.096888 | 0.426661 |
| C 19.9175573889 | 11.41258423 | 17.2982107426 C | -2.637841 | -3.089412 | -0.102977 |
| H 20.4727716757 | 11.311811754 | 16.7585890595 H | -0.902066 | -3.65745 | 2.765093 |
| H 22.5078414036 | 10.8976209049 | 18.0798056248 H | -2.484928 | -2.96748 | -1.176155 |
| H 22.9145180047 | 8.5632364961 | 18.85546234 C | -1.573744 | -0.328957 | -1.676711 |
| H 21.2454896182 | 6.7862519871 | 18.3418614798 O | -2.528643 | -0.543516 | -2.283304 |
| H 19.180961159 | 7.339072274 | 17.0782940979 H | -1.019035 | -0.651965 | 0.515732 |
| C 14.3124766967 | 9.6477290168 | 14.0381273872 C | 1.140983 | -0.037195 | 0.789685 |
### 6\(^{th}\) Charge = 0, Multiplicity = 1

$$E(R_{HoB97XD}) = -3368.90711089$$

| Element | Atomic Number | Atomic Weight | Charge | Multiplicity | E(R\(_{HoB97XD}\)) | DeltaE | DeltaE/\((\text{amu}^{-1})\) |
|---------|---------------|---------------|--------|--------------|-----------------|--------|-----------------|
| C       | 6             | 12.01074      | 0      | 1            | -3368.90711089  |        |                 |
| Cr      | 24            | 52.00527      | 0      | 1            | -1335.00000801  | -1533.90711089 | -1533.90711089 |
| O       | 8             | 15.99943      | 0      | 1            | -3368.90711089  |        |                 |
| P       | 15            | 30.97374      | -3     | 1            | -3368.90711089  |        |                 |
| N       | 7             | 14.00307      | -3     | 1            | -3368.90711089  |        |                 |
| H       | 1             | 1.00782       | 1      | 1            | -3368.90711089  |        |                 |

*Note: The table above lists the elements and their atomic numbers, charges, and Mulliken populations for the 6\(^{th}\) charge state.*
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