Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Synthesis of free and ligated 1,2-thiaphosphetanes – expanding the pool of strained P-ligands

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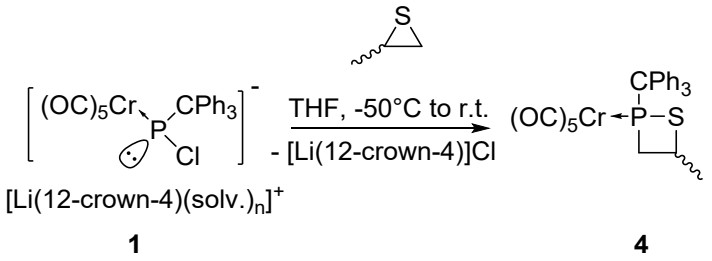
Content:

General procedures

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire/benzophenone and further purified by subsequent distillation. The purity of complexes **5** and **6** was established by elemental analysis as well as NMR spectroscopy. For compounds **4** and **7** the purity was only confirmed by NMR spectroscopy due to the low yields. All NMR spectra were recorded on a Bruker Avance I 400 MHz or a Bruker Avance III HD Prodigy 500 MHz spectrometer at 25 °C. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standards, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S apparatus; the values are uncorrected. Elemental analyses were carried out on a Vario EL elemental analyser. Mass spectrometric data were collected either on a MAT 95 XL Finnigan spectrometer using EI, 70 eV or a Thermo Finnigan MAT 90 sector instrument equipped with a LIFDI ion source (Linden CMS). IR spectra of all compounds were recorded on a Thermo Nicolet 380 FT-IR spectrometer with an attenuated total reflection (ATR) attachment or a Bruker Alpha Diamond ATR FTIR spectrometer.



Synthesis of complex **4**: 269 mg (0.5 mmol) of dichloro(organo)phosphane complex **1** were dissolved in 20 mL of THF in a 50 mL Schlenk tube and 75 µL (0.46 mmol) of 12-crown-4 (1,4,7,10-tetraoxacyclododecan) were added. The solution was then cooled to -80 °C and, subsequently, 0.35 mL (0.6 mmol) of a *tert*-butyl lithium solution (1.7 M in *n*-hexane) were added drop wise with continuous stirring. After slow warming to -55 °C 100 µL (1.3 mmol) of propylene sulfide were added while stirring continued.

The reaction mixture was allowed slowly warming to ambient temperature overnight, after which all volatiles were removed *in vacuo* (0.02 mbar). The product was extracted with three times 10 mL of *n*-pentane. The solvent was removed *in vacuo* (0.02 mbar) and the crude material was purified by washing with three times 2 mL of *n*-pentane. The product was obtained after drying *in vacuo* (0.02 mbar) as mixture of two isomers and all data are given for the mixture.

Yield: 17 mg (0.03 mmol, 6.5 %). Pale yellow solid. Isomeric ratio **Isomer 1**:**Isomer 2**: 40 : 60. **(Isomer 1) ^{1}H NMR** (500.2 MHz, $CDCl_3$) δ = 1.39 (d, 3 H, $^{3}J_{H,H}$ = 6.6 Hz, C*H*$_3$), 2.97 (ddd, 1 H, $^{2}J_{P,H}$ = 9.0 Hz, $^{2}J_{H,H}$ = 14.2 Hz, $^{3}J_{H,H}$ = 7.2 Hz, C*H*$_2$), 3.09 (ddd, 1 H, $^{2}J_{P,H}$ = 7.1 Hz, $^{2}J_{H,H}$ = 14.2 Hz, $^{3}J_{H,H}$ = 9.3 Hz, C*H*$_2$), 3.28 (ddq, 1 H, $^{3}J_{H,H}$ = 9.3 Hz, $^{3}J_{H,H}$ = 6.6 Hz, $^{3}J_{H,H}$ = 7.2 Hz, C*H*), 7.25 – 7.40 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ = 25.5 (d, $^{3}J_{P,C}$ = 7.4 Hz, *C*H$_3$), 39.4 (d, $^{2}J_{P,C}$ = 4.4 Hz, *C*H), 41.3 (d, $^{1}J_{P,C}$ = 25.9 Hz, P-*C*H$_2$), 67.0 (d, $^{1}J_{P,C}$ = 13.6 Hz, *C*Ph$_3$), 127.8 (s$_{br}$, *para*-*C*H), 128.4 (s$_{br}$, *C*H), 130.9 (s$_{br}$, *C*H), 142.0 (s$_{br}$, *ipso*-*C*), 215.5 (d, $^{2}J_{P,C}$ = 11.4 Hz, *cis*-*C*O), 221.5 (d, $^{2}J_{P,C}$ = 3.0 Hz, *trans*-*C*O). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$) δ = 120.2 (s). **(Isomer 2) ^{1}H NMR** (500.2 MHz, $CDCl_3$) δ = 0.97 (d, 3 H, $^{3}J_{H,H}$ = 6.6 Hz, C*H*$_3$), 2.64 (ddd, 1 H, $^{2}J_{P,H}$ = 11.0 Hz, $^{2}J_{H,H}$ = 13.1 Hz, $^{3}J_{H,H}$ =

8.0 Hz, CH_2), 3.03 (ddd, 1 H, $^2J_{P,H}$ = 7.1 Hz, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 8.0 Hz, CH_2), 4.19 (dddq, 1 H, $^3J_{P,H}$ = 2.0 Hz, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 6.6 Hz, C*H*), 7.25 – 7.40 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ = 25.6 (s, *C*H_3), 36.0 (d, $^2J_{P,C}$ = 4.4 Hz, *C*H), 41.3 (d, $^1J_{P,C}$ = 21.3 Hz, *C*H_2), 68.1 (d, $^1J_{P,C}$ = 14.7 Hz, *C*Ph_3), 127.9 (s, *para-C*H), 128.4 (s_{br}, *C*H), 131.2 (d, $J_{P,C}$ = 7.0 Hz, *C*H), 141.6 (s, *ipso-C*), 215.5 (d, $^2J_{P,C}$ = 11.7 Hz, *cis-C*O), 221.2 (d, $^2J_{P,C}$ = 3.3 Hz, *trans-C*O). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$) δ = 104.2 (s). **MS** (lifdi) m/z (%) = 540.0 (100) $[M]^{\bullet+}$, 296.9 (3) $[M - CPh_3]^+$, 243.1 (20) $[CPh_3]^+$. **IR** (ATR, $\tilde{\upsilon}$ [cm^{-1}]) $\tilde{\upsilon}$ = 2061 (s, ν(CO)), 1989 (w, ν(CO)), 1936 (vs, ν(CO)).

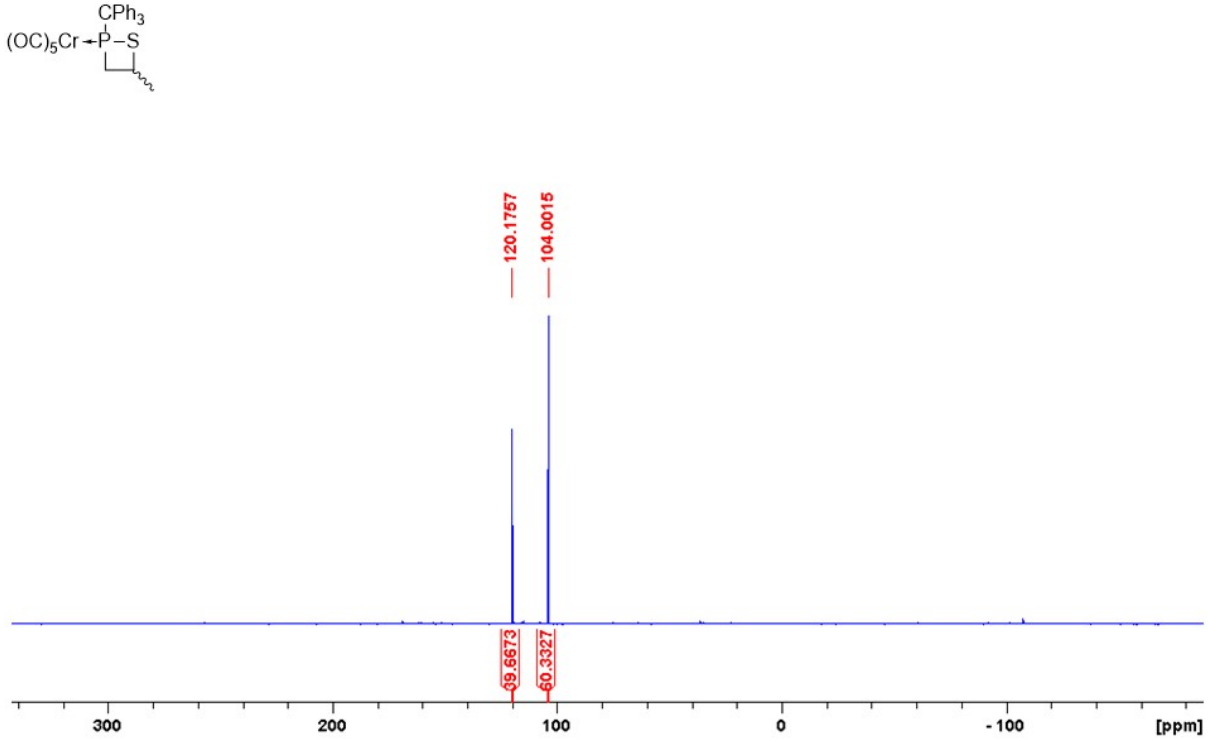


Figure S1. ^{31}P{^{1}H} NMR spectrum of **4**.

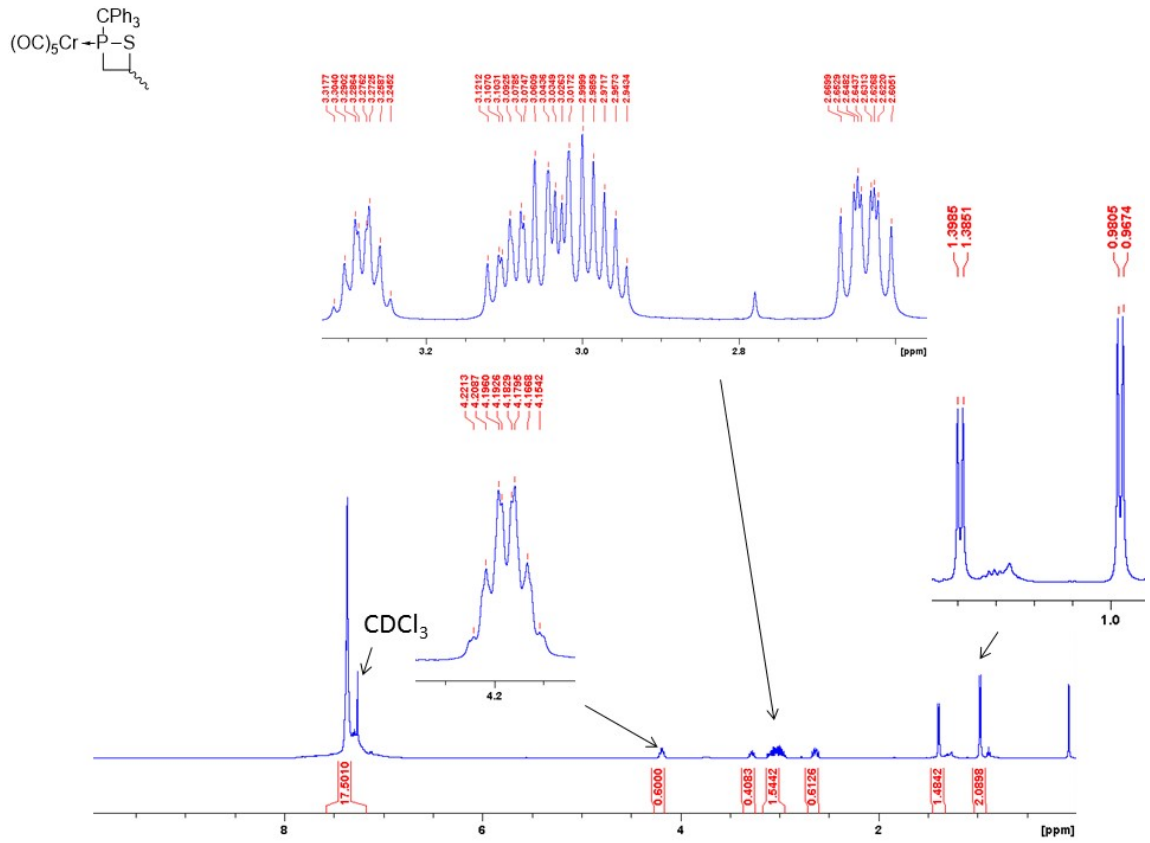


Figure S2. ^{1}H NMR spectrum of **4**.

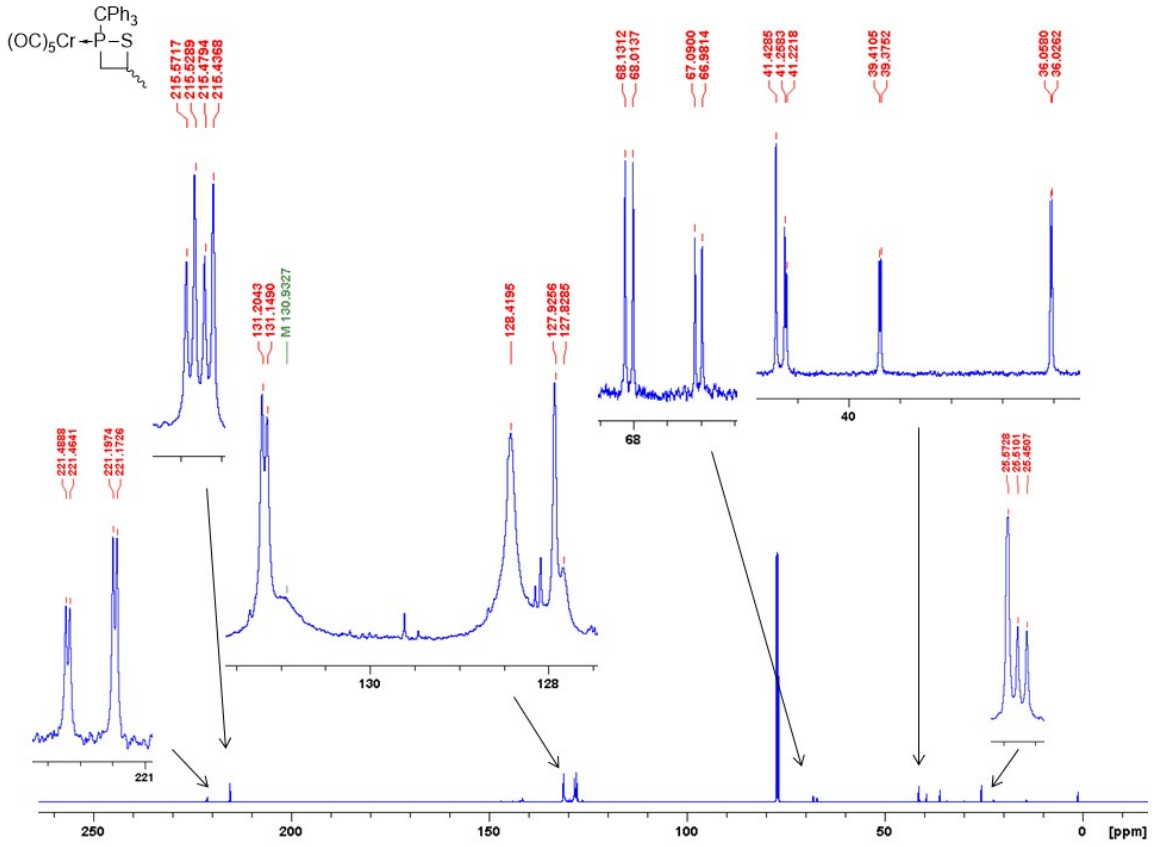
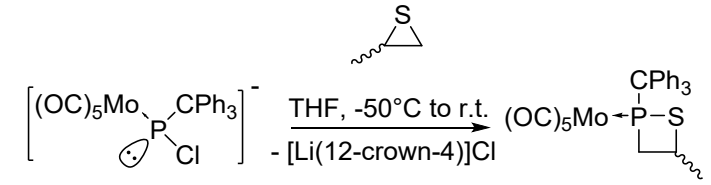


Figure S3. ^{13}C{^{1}H} NMR spectrum of **4**.



2 **5**

Synthesis of complex **5**: 1.152 g (2.0 mmol) of the P-$Mo(CO)_5$ substituted dichloro(organo)phosphane complex **2** were dissolved in 30 mL of THF in a 50 mL Schlenk tube and 320 µL (2.0 mmol) of 12-crown-4 (1,4,7,10-tetraoxacyclododecan) were added. The solution was then cooled to -80 °C and, subsequently, 1.4 mL (2.4 mmol) of a *tert*-butyl lithium solution (1.7 M in *n*-hexane) were added drop wise with continuous stirring. After slow warming to -50 °C, 250 µL (3.56 mmol) of propene sulfide were added while stirring continued.

The reaction mixture was allowed slowly warming to ambient temperature overnight. All volatiles were removed in *vacuo* (0.02 mbar). The formed salt was separated by filtration over Al_2O_3 (d = 2 cm, h = 3 cm, Et_2O), the solvent was removed *in vacuo* (0.02 mbar) and the crude material was purified by washing with two times 2 mL of diethyl ether at 0°C. The product was obtained as mixture of two isomers and all data are given for the mixture.

Yield: 370 mg (0.640 mmol, 32 %). White solid, m.p.: 160-165 °C (dec.). Isomeric ratio **Isomer 1**:**Isomer 2**: 41 :59. **(Isomer 1)** **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ = 1.42 (d, 3 H, $^3J_{H,H}$ = 6.7 Hz, CH_3), 3.02 (ddd, 1 H, $^2J_{P,H}$ = 7.8 Hz, $^2J_{H,H}$ = 14.1 Hz, $^3J_{H,H}$ = 7.4 Hz, CH_2), 3.10 (ddd, 1 H, $^2J_{P,H}$ = 6.6 Hz, $^2J_{H,H}$ = 14.1 Hz, $^3J_{H,H}$ = 9.2 Hz, CH_2), 3.38 (ddq, 1 H, $^3J_{H,H}$ = 9.2 Hz, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 6.7 Hz, C*H*), 7.11 – 7.41 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ = 26.1 (d, $^3J_{P,C}$ = 7.1 Hz, *C*H_3), 39.4 (d, $^2J_{P,C}$ = 3.8 Hz, *C*H), 41.2 (d, $^1J_{P,C}$ = 25.6 Hz, P-*C*H_2), 65.2 (d, $^1J_{P,C}$ = 14.2 Hz, *C*Ph_3), 127.8 (s_{br}, *para*-*C*H), 128.4 (s_{br}, *C*H), 130.7 (s_{br}, *C*H), 142.5 (s_{br}, *ipso*-*C*), 205.0 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-*C*O), 211.3 (d, $^2J_{P,C}$ = 32.5 Hz, *trans*-*C*O). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$) δ = 92.9 (s). **(Isomer 2)** **^{1}H NMR** (500.2 MHz, $CDCl_3$) δ = 1.04 (d, 3 H, $^3J_{H,H}$ = 6.8 Hz, CH_3), 2.62 (ddd, 1 H, $^2J_{P,H}$ = 10.5 Hz, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 8.7 Hz, CH_2), 3.00 (ddd, 1 H, $^2J_{P,H}$ = 10.2 Hz, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 7.8 Hz, CH_2), 4.21 (dddq, 1 H, $^3J_{P,H}$ = 1.6 Hz, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 6.8 Hz, C*H*), 7.11 – 7.41 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ = 25.7 (s, *C*H_3), 35.5 (d, $^2J_{P,C}$ = 3.3 Hz, *C*H), 41.5 (d, $^1J_{P,C}$ = 20.4 Hz, *C*H_2), 66.2 (d, $^1J_{P,C}$ = 14.7 Hz, *C*Ph_3), 127.9 (s, *para*-*C*H), 128.4 (s_{br}, *C*H), 130.9 (d, $J_{P,C}$ = 7.7 Hz, *C*H), 141.7 (d, $^2J_{P,C}$ = 2.9 Hz, *ipso*-*C*), 204.9 (d, $^2J_{P,C}$ = 8.2 Hz, *cis*-*C*O), 210.8 (d, $^2J_{P,C}$ = 32.4 Hz, *trans*-*C*O). **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$) δ = 76.2 (s). **MS** (lifdi) m/z (%) = 558.9 (100) $[M]^{\bullet+}$, 342.8 (10) $[M - CPh_3]^+$, 243.1 (95) $[CPh_3]^+$. **IR** (ATR, $\tilde{\nu}$ [cm^{-1}]) $\tilde{\nu}$ = 2071 (s, ν(CO)), 1995 (s, ν(CO)), 1955 (s, ν(CO)), 1912 (vs, ν(CO)). **EA** calc. for $C_{27}H_{21}O_5PSMo$: C 55.49, H 3.62, S 5.49 found: C 55.91, H 3.75, S 5.16.

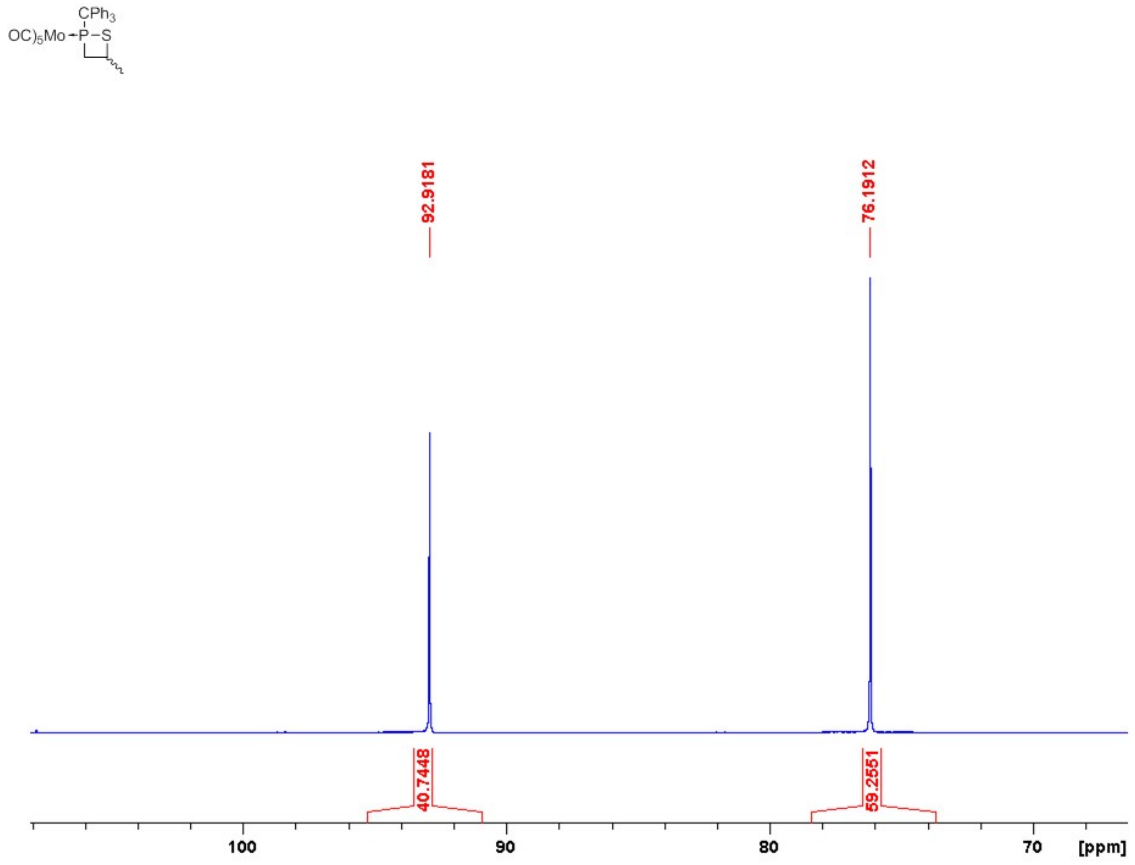


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **5**.

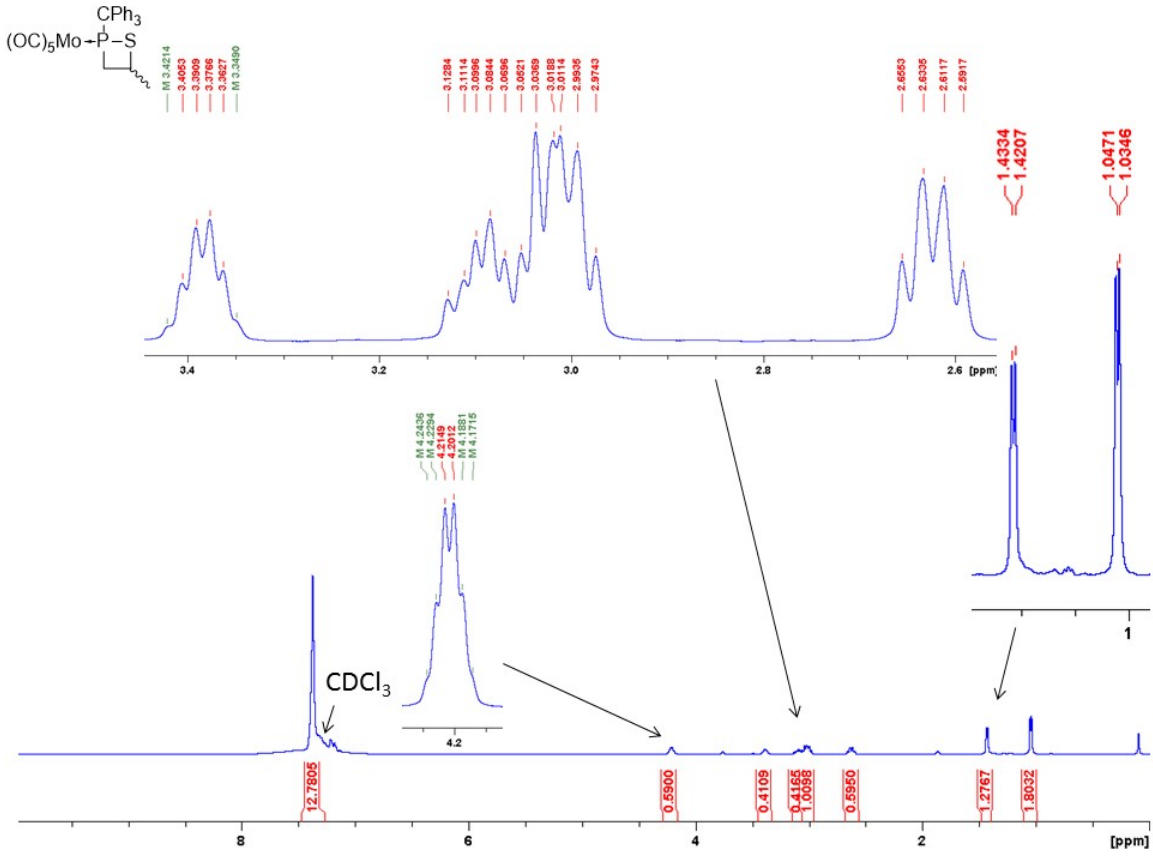


Figure S5. ^{1}H NMR spectrum of **5**.

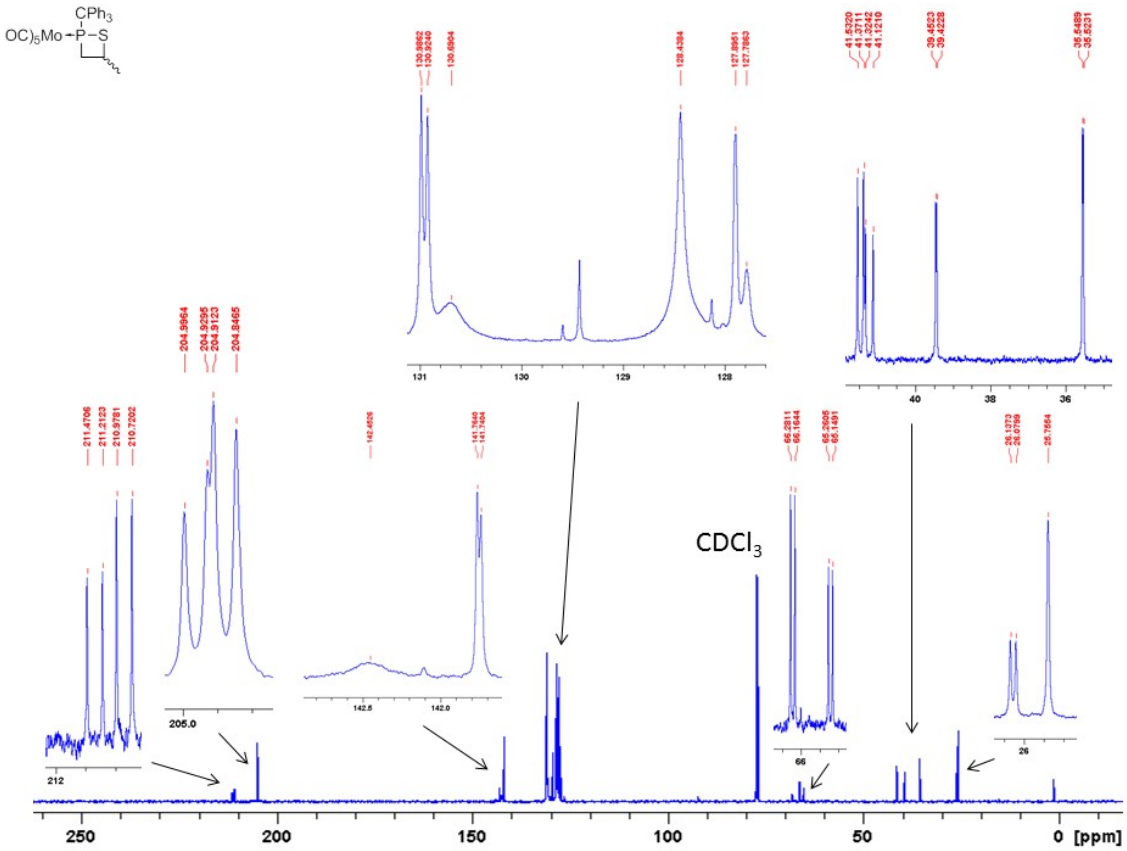
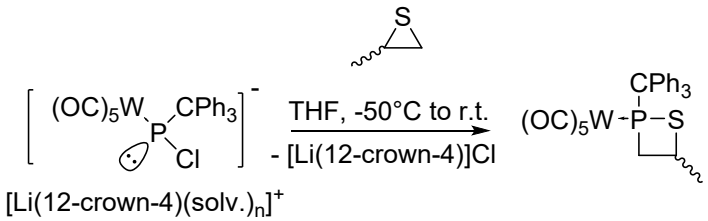


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.



3 **6**

Synthesis of complex **6**: 1.004 g (1.5 mmol) of the *P*-$W(CO)_5$ substituted dichloro(organo)phosphane complex **3** were dissolved in 30 mL of THF in a 50 mL Schlenk tube and 240 µL (1.5 mmol) of 12-crown-4 (1,4,7,10-tetraoxacyclododecan) were added. The solution was then cooled to -80 °C and, subsequently, 0.96 mL (1.63 mmol) of a *tert*-butyl lithium solution (1.7 M in *n*-hexane) were added drop wise with continuous stirring. After slow warming to -50 °C 200 µL (2.85 mmol) of propene sulfide were added while stirring continued.

The reaction mixture was allowed slowly warming up to ambient temperature overnight. All volatiles were removed in *vacuo* (0.02 mbar). The formed salt was separated by filtration over Al_2O_3 (d = 2 cm, h = 5 cm, Et_2O), the solvent was removed *in vacuo* (0.02 mbar) and the crude material was purified by washing with three times 5 mL of petroleum ether at -50°C. The product was obtained as mixture of two isomers and all data are given for the mixture.

Yield: 390 mg (0.58 mmol, 39 %). White solid, m.p.: 138 °C. Isomeric ratio **Isomer 1**: **Isomer 2**: 44 :56. **(Isomer 1) ^{1}H NMR** (400.1 MHz, $CDCl_3$) δ = 1.43 (d, 3 H, $^{3}J_{H,H}$ = 6.6 Hz, CH_3), 3.18 (ddd, 1 H, $^{2}J_{P,H}$ = 8.6 Hz, $^{2}J_{H,H}$ = 14.2 Hz, $^{3}J_{H,H}$ = 7.8 Hz, CH_2), 3.25 (ddd, 1 H, $^{2}J_{P,H}$ = 6.7 Hz, $^{2}J_{H,H}$ = 14.2 Hz, $^{3}J_{H,H}$ = 8.9 Hz, CH_2), 3.43 (ddq, 1 H, $^{3}J_{H,H}$ = 8.5 Hz, $^{3}J_{H,H}$ = 7.8 Hz, $^{3}J_{H,H}$ = 6.6 Hz, C*H*), 7.25 – 7.45

(m, 15 H, Ph). **^{13}C{^{1}H} NMR** (100.7 MHz, $CDCl_3$) δ = 25.7 (s_{br}, *C*H_3), 39.1 (d, $^{2}J_{P,C}$ = 5.2 Hz, *C*H), 42.1 (d, $^{1}J_{P,C}$ = 29.7 Hz, P-*C*H_2), 65.3 (d, $^{1}J_{P,C}$ = 8.6 Hz, *C*Ph_3), 127.8 (s_{br}, *para*-*C*H), 128.4 (s_{br}, *C*H), 130.8 (s_{br}, *C*H), 142.3 (s_{br}, *ipso*-*C*), 197.5 (d_{sat}, $^{1}J_{W,C}$ = 127.6 Hz, $^{2}J_{P,C}$ = 6.5 Hz, *cis*-*C*O), 200.0 (d, $^{2}J_{P,C}$ = 31.5 Hz, *trans*-*C*O). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$) δ = 65.3 (s_{sat}, $^{1}J_{W,P}$ = 256.7 Hz). **(Isomer 2)** **^{1}H NMR** (400.1 MHz, $CDCl_3$) δ = 1.05 (d, 3 H, $^{3}J_{H,H}$ = 6.6 Hz, C*H*$_3$), 2.85 (ddd, 1 H, $^{2}J_{P,H}$ = 11.1 Hz, $^{2}J_{H,H}$ = 13.0 Hz, $^{3}J_{H,H}$ = 8.6 Hz, C*H*$_2$), 3.15 (ddd, 1 H, $^{2}J_{P,H}$ = 8.0 Hz, $^{2}J_{H,H}$ = 13.0 Hz, $^{3}J_{H,H}$ = 7.9 Hz, C*H*$_2$), 4.20 (dddq, 1 H, $^{3}J_{P,H}$ = 2.0 Hz, $^{3}J_{H,H}$ = 8.6 Hz, $^{3}J_{H,H}$ = 7.9 Hz, $^{3}J_{H,H}$ = 6.6 Hz, C*H*), 7.25 – 7.45 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (100.7 MHz, $CDCl_3$) δ = 25.8 (s_{br}, *C*H_3), 35.6 (d, $^{2}J_{P,C}$ = 4.5 Hz, *C*H), 42.6 (d, $^{1}J_{P,C}$ = 24.6 Hz, *C*H_2), 66.3 (d, $^{1}J_{P,C}$ = 9.3 Hz, *C*Ph_3), 128.0 (s_{br}, *para*-*C*H), 128.4 (s_{br}, *C*H), 131.1 (d, $J_{P,C}$ = 7.7 Hz, *C*H), 141.6 (d, $^{2}J_{P,C}$ = 2.7 Hz, *ipso*-*C*), 197.2 (d_{sat}, $^{1}J_{W,C}$ = 127.4 Hz, $^{2}J_{P,C}$ = 6.5 Hz, *cis*-*C*O), 199.5 (d, $^{2}J_{P,C}$ = 31.7 Hz, *trans*-*C*O). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$) δ = 50.5 (s_{sat}, $^{1}J_{W,P}$ = 254.6 Hz). **MS** (EI, 70 eV, ^{184}W) m/z (%) = 672.1 (2) $[M]^{\bullet+}$, 546.0 (8) $[M - 3\ CO - C_3H_6]^+$, 490.0 (65) $[M - 5\ CO - C_3H_6]^+$, 243.1 (100) $[CPh_3]^+$, 165.0 (30) $[CPh_3 - C_6H_6]^+$. **IR** (ATR, ṽ [cm^{-1}]) ṽ = 2070 (s, ν(CO)), 1984 (m, ν(CO)), 1910 (vs, ν(CO)). **EA** calc. for $C_{27}H_{21}O_5PSW$: C 48.23, H 3.15, S 4.77 found: C 48.54, H 3.20, S 4.79.

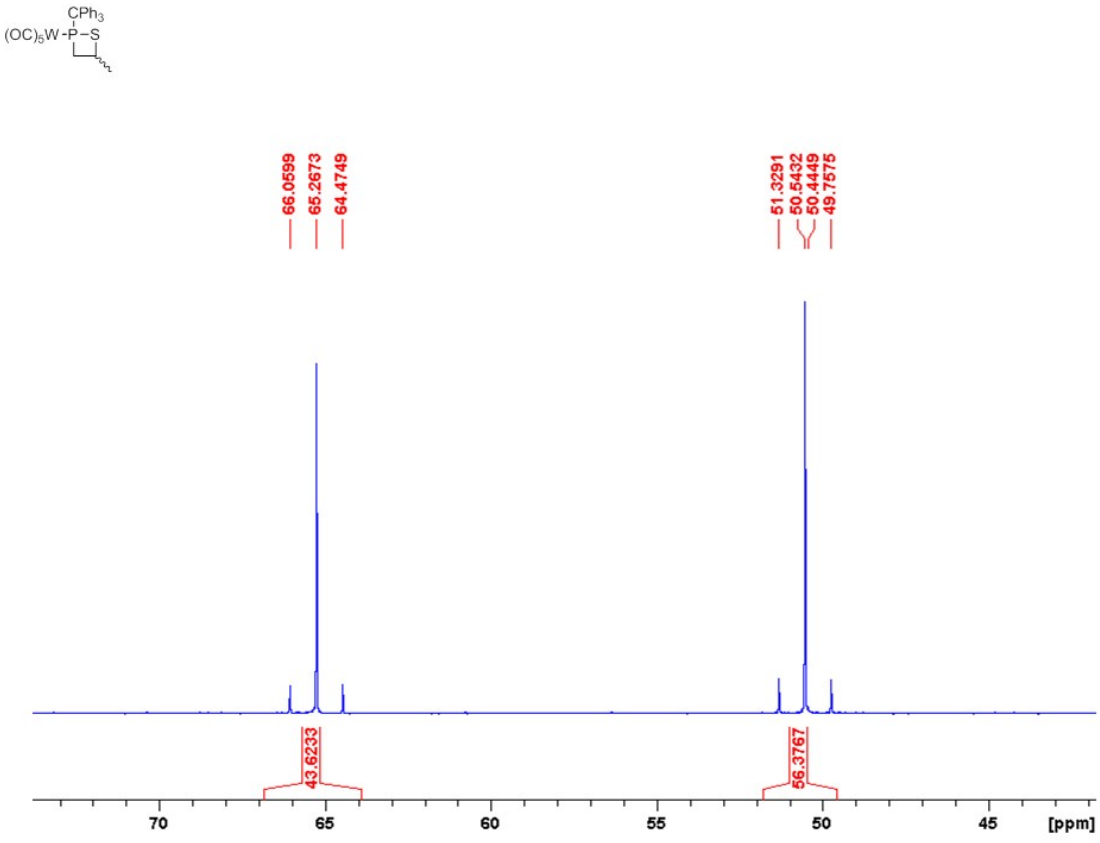


Figure S7. ^{31}P{^{1}H} NMR spectrum of **6**.

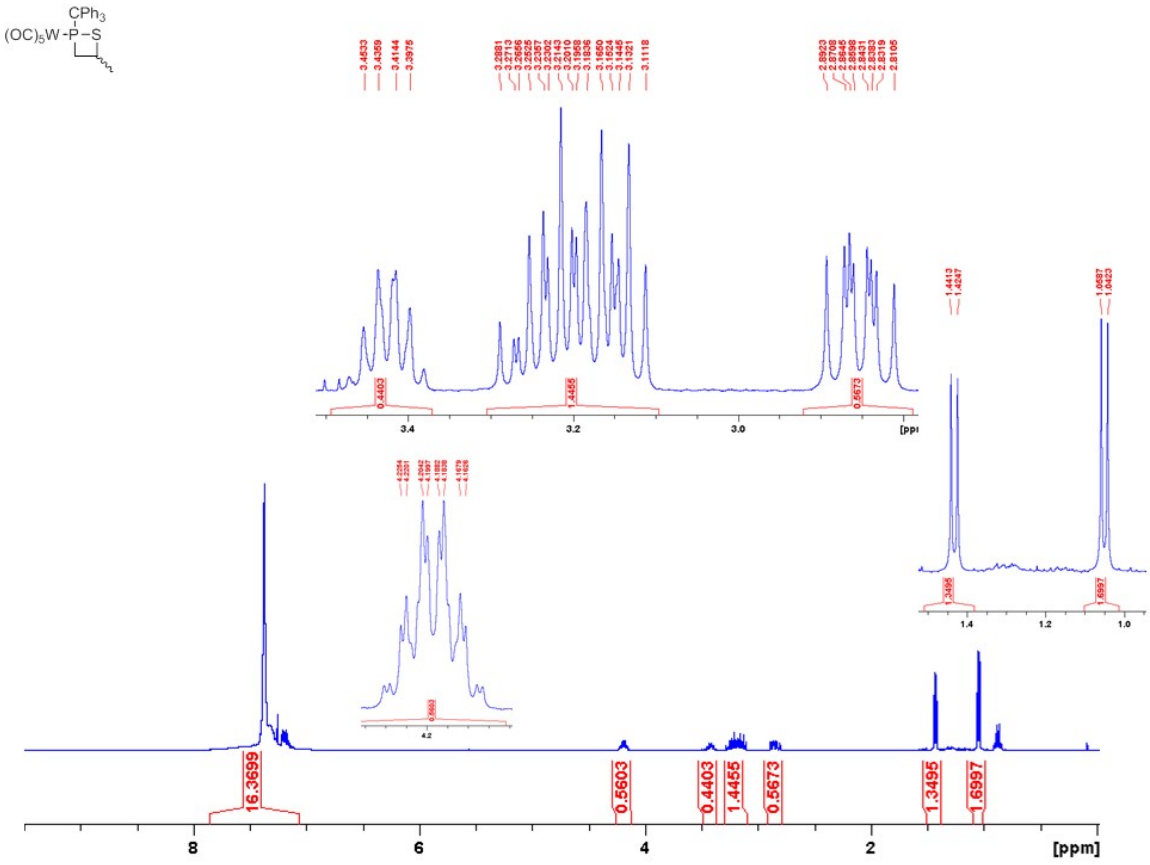


Figure S8. ^{1}H NMR spectrum of **6**.

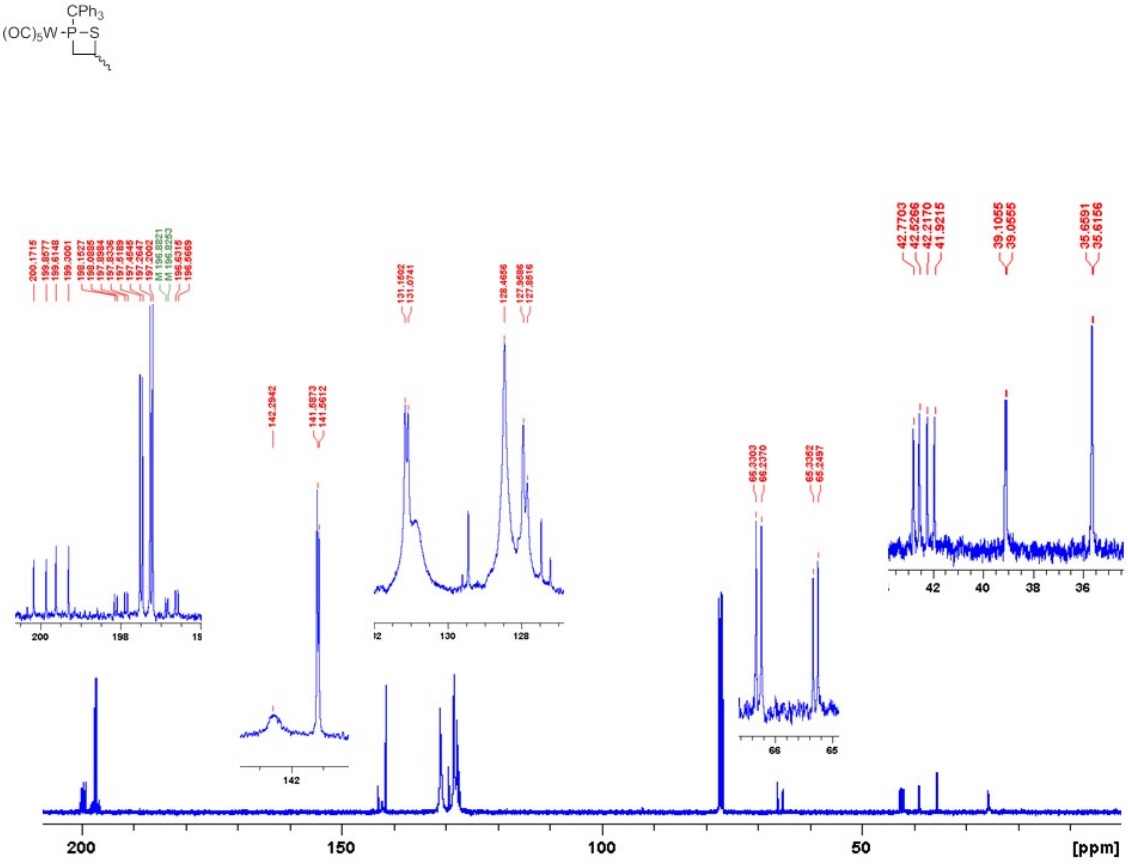
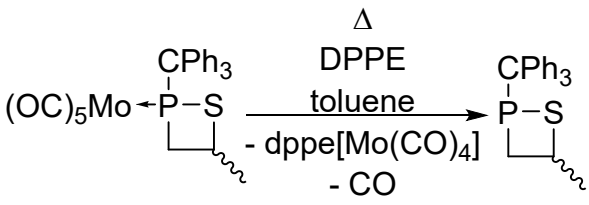


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.



5 **7**

Synthesis of **7**: 219 mg (0.375 mmol) of 1,2-thiaphosphetane complexes **5** and 146 mg (0.375 mmol) of DPPE were dissolved in 30 mL of toluene in a 100 mL Schlenk tube and the mixture was heated to 80 °C for 20 h. All volatiles were removed *in vacuo* (0.02 mbar) and the residue extracted with a mixture of diethyl ether and *n*-pentane (1:1) at -35 °C. Subsequent removal of the solvent (0.02 mbar) led to the crude product as a yellow powder. The product was purified by crystallization from the diethyl ether/ *n*-pentane mixture. Only a small amount of the purified compound was obtained as a mixture of two isomers, all data are given for the mixture.

Yield: 7 mg (0.02 mmol, 5 %). Yellow solid. Isomeric ratio **Isomer 1**: **Isomer 2**: 57 : 43. (**Isomer 1**) **^{1}H NMR** (400.1 MHz, $CDCl_3$) δ = 1.32 (d, 3 H, $^{3}J_{H,H}$ = 6.7 Hz, CH_3), 2.33 (dd, 1 H, $^{2}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 9.4 Hz, CH_2), 2.55 (ddd, 1 H, $^{2}J_{P,H}$ = 28.4 Hz, $^{2}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 6.6 Hz, CH_2), 3.21 (ddq, 1 H, $^{3}J_{H,H}$ = 9.4 Hz, $^{3}J_{H,H}$ = 6.6 Hz, $^{3}J_{H,H}$ = 6.7 Hz, C*H*), 7.21 – 7.42 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$) δ = 28.4 (d, $^{3}J_{P,C}$ = 2.2 Hz, *C*H_3), 30.1 (d, $^{1}J_{P,C}$ = 7.5 Hz, P-*C*H_2), 40.1 (d, $^{2}J_{P,C}$ = 9.5 Hz, *C*H), 60.2 (d, $^{1}J_{P,C}$ = 52.8 Hz, *C*Ph_3), 126.6 (d, $^{5}J_{P,C}$ = 1.5 Hz, *para*-*C*H), 128.2 (s, *C*H), 129.7 (d, $J_{P,C}$ = 10.8 Hz, *C*H), 144.3 (d, $^{2}J_{P,C}$ = 9.3 Hz, *ipso*-*C*). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$) δ = 74.5 ppm (s). (**Isomer 2**) **^{1}H NMR** (400.1 MHz, $CDCl_3$) δ = 0.97 (d, 3 H, $^{3}J_{H,H}$ = 6.7 Hz, CH_3), 1.96 (dd, 1 H, $^{2}J_{H,H}$ = 12.6 Hz, $^{3}J_{H,H}$ = 9.2 Hz, CH_2), 2.67 (ddd, 1 H, $^{2}J_{P,H}$ = 28.0 Hz, $^{2}J_{H,H}$ = 12.6 Hz, $^{3}J_{H,H}$ = 7.4 Hz, CH_2), 3.91 (ddq, 1 H, $^{3}J_{H,H}$ = 8.9 Hz, $^{3}J_{H,H}$ = 7.4 Hz, $^{3}J_{H,H}$ = 6.7 Hz, C*H*), 7.21 – 7.42 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$) δ = 27.4 (d, $^{3}J_{P,C}$ = 5.6 Hz, *C*H_3), 32.5 (d, $^{1}J_{P,C}$ = 13.8 Hz, *C*H_2), 35.1 (d, $^{2}J_{P,C}$ = 6.3 Hz, *C*H), 61.2 (d, $^{1}J_{P,C}$ = 52.8 Hz, *C*Ph_3), 126.9 (d, $^{5}J_{P,C}$ = 1.5 Hz, *para*-*C*H), 128.2 (s, *C*H), 129.9 (d, $J_{P,C}$ = 9.9 Hz, *C*H), 143.8 (d, $^{2}J_{P,C}$ = 9.3 Hz, *ipso*-*C*). **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$) δ = 47.7 ppm (s).

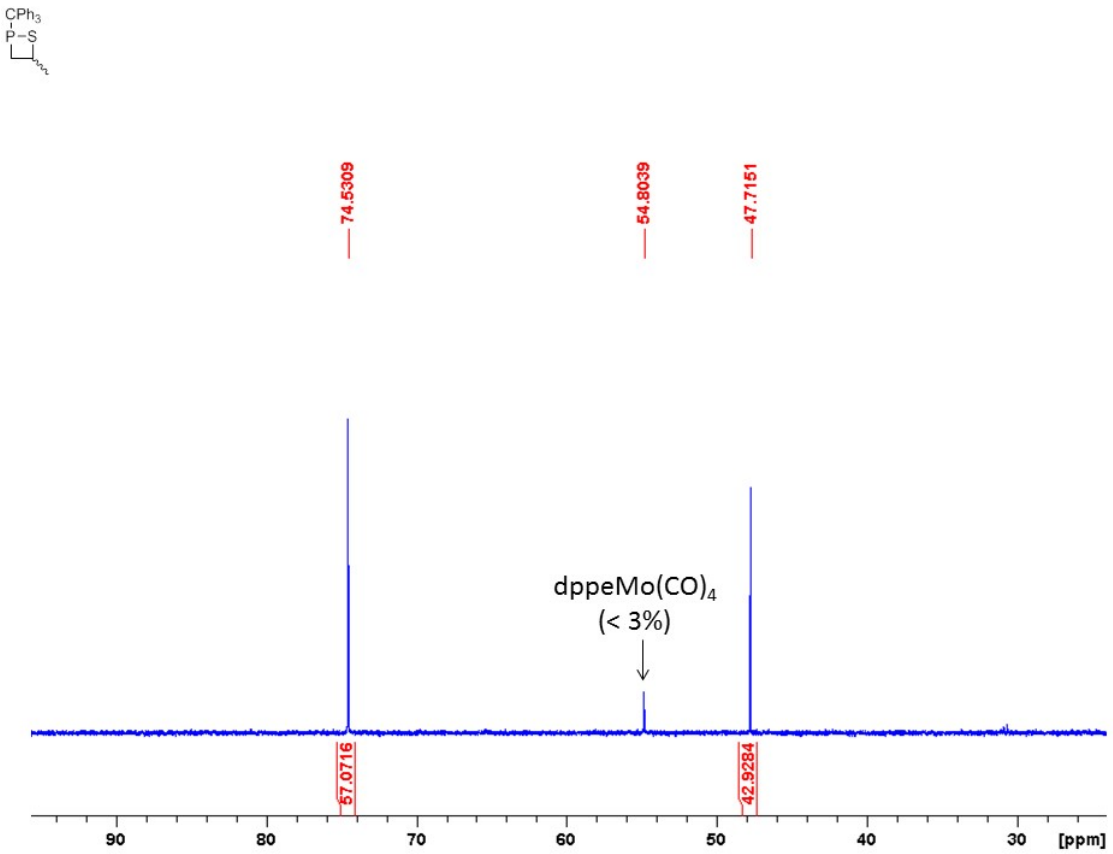


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **7**.

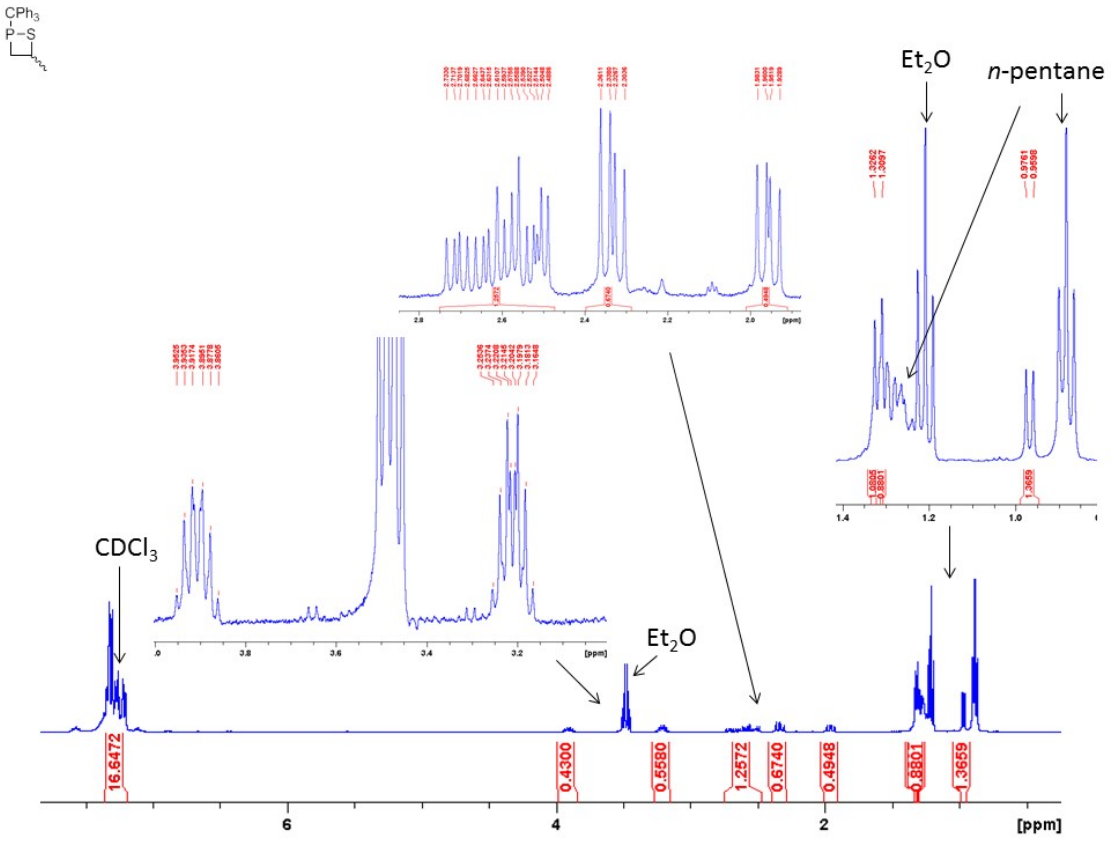


Figure S11. ^{1}H NMR spectrum of **7**.

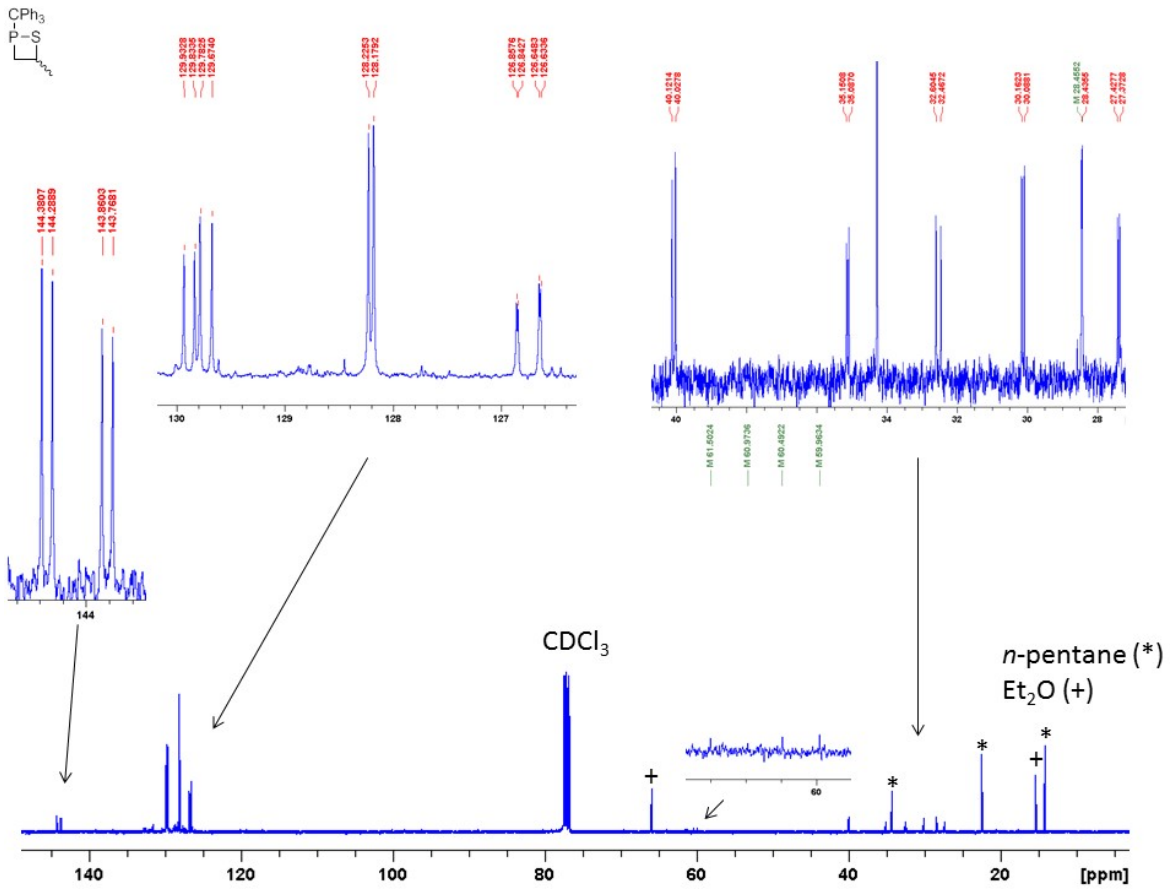
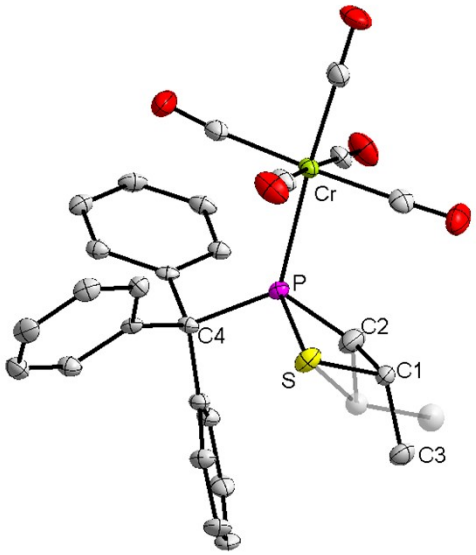


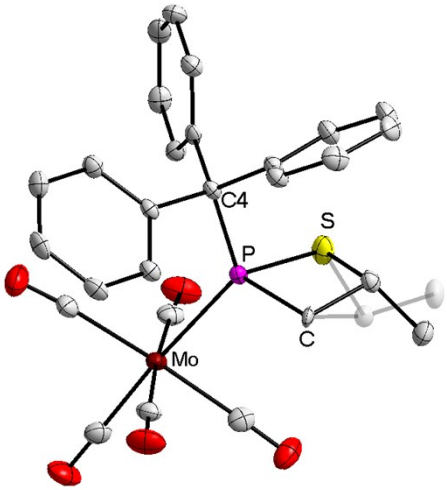
Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **7**.

X-ray crystallographic analyses of 4, 5, 6 and 7

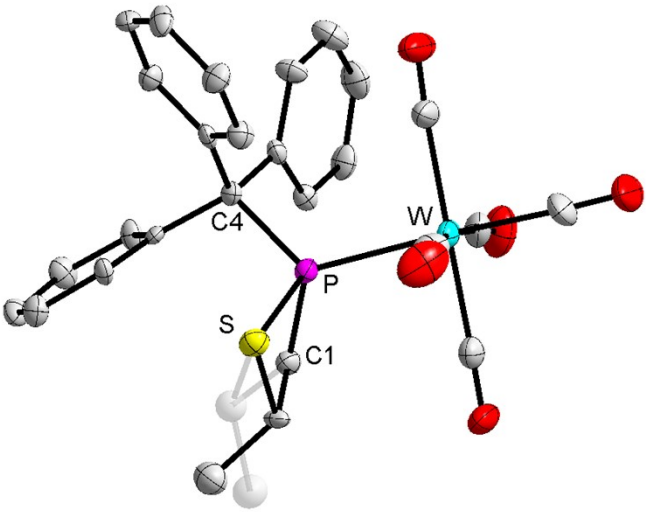
Suitable single crystals were obtained from concentrated diethyl ether (**4**, **5** and **6**) solutions upon slow evaporation of the solvent at 4°C or a mixture of diethyl ether/ n-pentane (**7**) upon slow evaporation at ambient temperature. Data were collected on a Bruker X8-KappaApexII (**4**, **5, 6**) or Bruker D8-Venture (**7**) diffractometer equipped with a low-temperature device (Cryostream, Oxford Cryosystems) at 100 K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97[1]) and refined by full-matrix least squares on F^2 (SHELXL-97[1], SHELXL-2015[2] or OLEX2[3]). All non-hydrogens were refined anisotropically. The hydrogen atoms were included isotropically using the riding model on the bound atoms. Absorption corrections were carried out empirical (min./max. transmissions = 0.6459/0.7461 (**4**), 0.6770/0.7461 (**5**), 0.5126/0.7459 (**6**), 0.2059/0.7536 (**7**)).
Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1883419 (**4**), CCDC 1883418 (**5**), CCDC 1883417 (**6**), CCDC 1883420 (**7**). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.



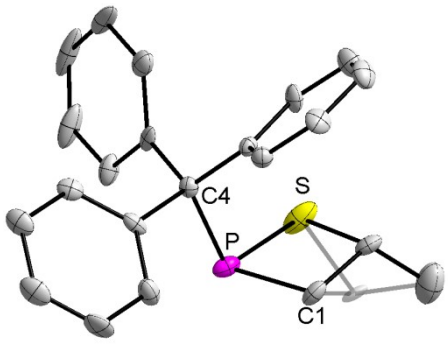
Crystal structure data of complex 4 ($C_{27}H_{21}O_5PSCr$): crystal size 0.18 x 0.12 x 0.06 mm, monoclinic, $P2_1/n$, a = 11.9943(5), b = 13.8498(5), c = 15.1345(7) Å, α = 90, β = 102.337(2), γ = 90°, V = 2456.07(18) Å^3, Z = 4, ρ_{calc} = 1.462 Mg m^{-3}, $2\theta_{max}$ = 55.996 °, collected (independent) reflections = 46113 (5905), R_{int} = 0.0597, μ = 0.653 mm^{-1}, 338 refined parameters, 48 restraints, R_1 (for I > 2σ(I)) = 0.0436, wR_2 (for all data) = 0.0940, max./min. residual electron density = 0.46/-0.47 e · Å^{-3}.



Crystal structure data of complex 5 ($C_{27}H_{21}O_5PSMo$): crystal size 0.2 x 0.12 x 0.04 mm, monoclinic, $P2_1/n$, a = 12.1584(6), b = 13.9761(6), c = 15.1772(8) Å, α = 90, β = 102.748(3), γ = 90°, V = 2515.4(2) Å^3, Z = 4, ρ_{calc} = 1.543 Mg m^{-3}, $2\theta_{max}$ = 55.996 °, collected (independent) reflections = 88820 (6070), R_{int} = 0.0557, μ = 0.704 mm^{-1}, 337 refined parameters, 7 restraints, R_1 (for I > 2σ(I)) = 0.0394, *w*R_2 (for all data) = 0.0835, max./min. residual electron density = 0.97/-0.77 e · Å^{-3}.



Crystal structure data of complex 6 ($C_{27}H_{21}O_5PSW$): crystal size 0.08 x 0.04 x 0.01 mm, monoclinic, $P2_1/c$, a = 10.8752(8), b = 44.889(3), c = 16.0622(12) Å, α = 90, β = 90.964(3), γ = 90°, V = 7840.0(10) Å^3, Z = 12, ρ_{calc} = 1.709 Mg m^{-3}, $2\theta_{max}$ = 56 °, collected (independent) reflections = 107550 (18901), R_{int} = 0.1095, μ = 4.596 mm^{-1}, 1009 refined parameters, 54 restraints, R_1 (for I > 2σ(I)) = 0.0559, *w*R_2 (for all data) = 0.1168, max./min. residual electron density = 1.39/-2.57 e · Å^{-3}.

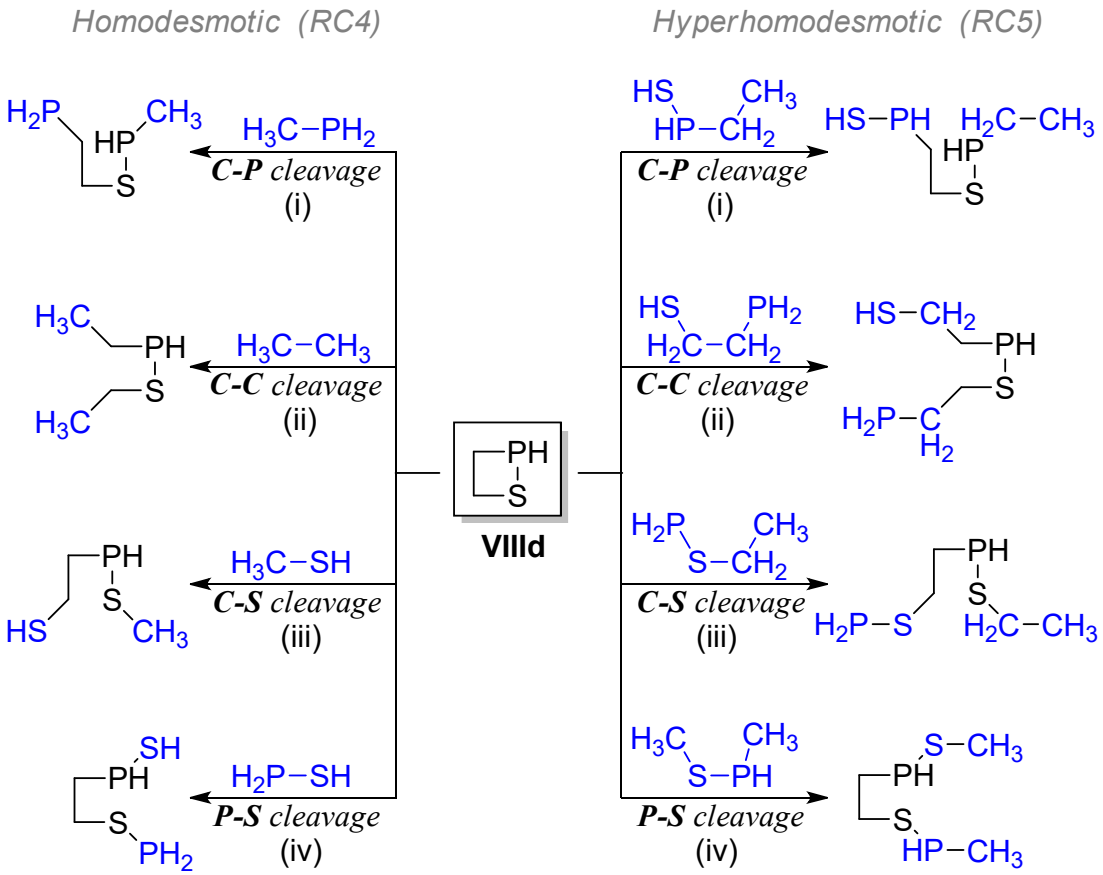


Crystal structure data of 7 ($C_{22}H_{21}PS$): crystal size 0.25 x 0.12 x 0.09 mm, orthorombic, $Pna2_1$, a = 8.9436(2), b = 19.1201(5), c = 10.6304(2) Å, α = 90, β = 90, γ = 90°, V = 1817.83(7) Å^3, Z = 4, ρ_{calc} = 1.273 Mg m^{-3}, $2\theta_{max}$ = 134.95 °, collected (independent) reflections = 28097 (3207), R_{int} = 0.0743, μ = 2.386 mm^{-1}, 229 refined parameters, 7 restraints, R_1 (for I > 2σ(I)) = 0.0656, *w*R_2 (for all data) = 0.1670, max./min. residual electron density = 0.56/-1.12 e · Å^{-3}.

Computational details.

DFT calculations were performed with the ORCA program.[4] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria in the gas-phase, using the B3LYP functional[5] together with the def2-TZVP basis set.[6] Effective core potential (ECP) was used for Mo [SD(28,MWB)],[7] and W [SD(60,MWB)]][7] atoms. The latest Grimme's semiempirical atom-pair-wise London dispersion correction (DFT-D3) was included in all calculations.[8] Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. From these optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP[9] basis set. Reported energies were corrected for the zero-point vibrational term at the optimization level. Final energies were obtained by means of the the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method[10] to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)).

RSEs were computed for the parent 1,2-thiaphosphetane **VIIId** at the above mentioned CCSD(T)/def2-TZVPP//B3LYP-D3/def2-TZVP level using the following homodesmotic and hyperhomodesmotic reactions (Scheme S1):



Scheme S1: Homodesmotic and hyperhomodesmotic reactions used in the RSE evaluation for parent thiaphosphetane **VIIId**.

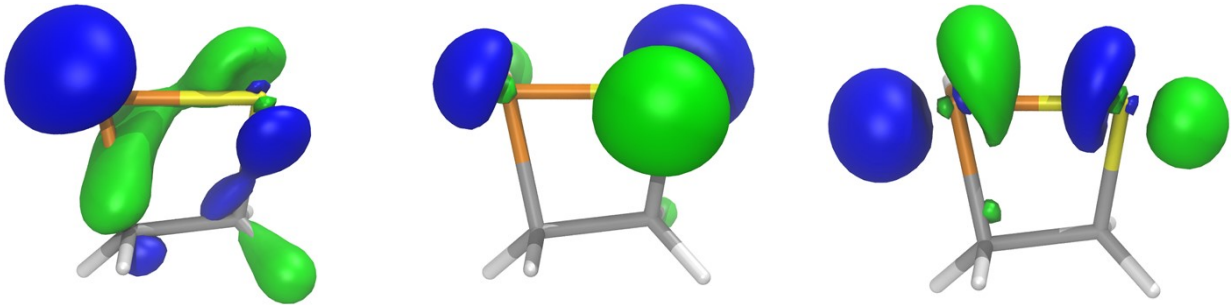


Figure S13: Computed (B3LYP-D3/def2-TZVPP) Kohn-Sham representative isosurfaces (isovalue 0.08 au) for parent thiaphosphetane **VIIId**.

Calculated structures.

Cartesian coordinates (in Å), ZPE- and G-correction (hartrees) for all computed species at the optimization level. Electronic energies (hartrees) at the DLPNO-CCSD(T)/def2-TZVPPecp level unless otherwise stated.

VIa E = -2427.156431474 au

ZPE = 0.11092581 au

G_{corr} = 0.06564649 au

Cr	0.059127	-0.038228	2.502631	O	1.193495	-2.864975	2.551266
C	0.078744	0.024244	4.391595	P	0.027994	-0.180068	0.193953
O	0.088787	0.055605	5.534001	H	1.267137	-0.072365	-0.485141
C	1.824171	0.676778	2.412566	S	-1.237564	0.983303	-1.076780
O	2.882028	1.100811	2.337361	C	-1.221467	-0.653693	-1.955944
C	-0.662921	1.730222	2.409911	H	-2.205568	-0.899346	-2.349647
O	-1.097480	2.782501	2.334774	H	-0.501441	-0.620108	-2.772224
C	-1.706220	-0.749286	2.501874	C	-0.745112	-1.542434	-0.795256
O	-2.762811	-1.184846	2.483155	H	-0.081197	-2.361983	-1.068114
C	0.770501	-1.802427	2.537923	H	-1.588212	-1.938218	-0.229719

TS(**VIa→VIIa**) E = -2427.103476122 au

ZPE = 0.10883891 au

G_{corr} = 0.06300276 au

$\bar{\upsilon}$ = -153.96 cm^{-1}

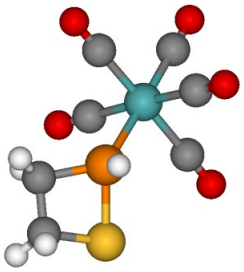
Cr	-0.120175	-0.046076	0.299669	O	-2.421508	-2.045014	0.577231
C	0.115493	-0.050326	2.129871	P	-1.266611	0.255575	-2.592240
O	0.260355	-0.053856	3.268846	H	-1.748782	-0.117506	-3.882523
C	1.154569	-1.474672	0.134842	S	0.836145	-0.158876	-2.892650
O	1.929508	-2.310423	0.089796	C	0.706481	1.525963	-3.656800
C	1.297032	1.217090	0.067919	H	1.556662	2.153388	-3.394208
O	2.138469	1.979946	-0.057229	H	0.658755	1.411521	-4.739464
C	-1.367197	1.386715	0.482011	C	-0.636956	1.959212	-3.056433
O	-2.102616	2.250009	0.627859	H	-1.282316	2.523471	-3.727985
C	-1.561809	-1.305684	0.450768	H	-0.500453	2.530627	-2.139704

VIIa E = -2427.135970013 au

ZPE = 0.11027424 au

G_{corr} = 0.06527783 au

Cr	0.059127	-0.038228	2.502631	O	1.193495	-2.864975	2.551266
C	0.078744	0.024244	4.391595	P	0.027994	-0.180068	0.193953
O	0.088787	0.055605	5.534001	H	1.267137	-0.072365	-0.485141
C	1.824171	0.676778	2.412566	S	-1.237564	0.983303	-1.076780
O	2.882028	1.100811	2.337361	C	-1.221467	-0.653693	-1.955944
C	-0.662921	1.730222	2.409911	H	-2.205568	-0.899346	-2.349647
O	-1.097480	2.782501	2.334774	H	-0.501441	-0.620108	-2.772224
C	-1.706220	-0.749286	2.501874	C	-0.745112	-1.542434	-0.795256
O	-2.762811	-1.184846	2.483155	H	-0.081197	-2.361983	-1.068114
C	0.770501	-1.802427	2.537923	H	-1.588212	-1.938218	-0.229719



VIIb E = -1451.469938712 au

ZPE = 0.10918616 au

G_{corr} = 0.06212816 au

Mo	0.074149	-0.040324	2.554041	O	1.261056	-3.007150	2.684772
C	0.092835	0.056619	4.588200	P	0.034705	-0.207451	0.095108
O	0.102713	0.104373	5.730032	H	1.270650	-0.140004	-0.595314
C	1.983558	0.722484	2.446297	S	-1.201702	0.992501	-1.173997
O	3.042388	1.140159	2.358410	C	-1.234175	-0.642672	-2.054811
C	-0.703587	1.870278	2.440102	H	-2.223411	-0.858277	-2.453366
O	-1.137757	2.921729	2.362294	H	-0.509430	-0.631213	-2.867736
C	-1.831818	-0.808196	2.554899	C	-0.789130	-1.543937	-0.892047
O	-2.887814	-1.243260	2.525846	H	-0.155746	-2.388299	-1.162390
C	0.839179	-1.946124	2.640423	H	-1.644673	-1.905750	-0.322578

TS(**VIb** normal retro [2+2]) E = -1451.393135526 au

ZPE = 0.106217830 au

G_{corr} = 0.05901591 au

$\tilde{\upsilon}$ = -504.48 cm^{-1}

Mo	-0.006879	-0.040758	2.455736	O	1.188400	-2.993864	2.244122
C	0.142511	-0.001029	4.496795	P	-0.076034	0.080182	0.009483
O	0.235742	0.025071	5.634352	H	1.134962	-0.233528	-0.654491
C	1.901754	0.723115	2.300690	S	-0.964769	1.524617	-1.074378
O	2.958253	1.140227	2.196609	C	-1.053831	-1.026933	-1.978608
C	-0.802555	1.876381	2.491299	H	-2.019937	-0.655843	-2.277201
O	-1.244043	2.923679	2.526255	H	-0.255230	-0.931600	-2.701803
C	-1.922325	-0.797028	2.525973	C	-0.863057	-1.698276	-0.769673
O	-2.981989	-1.221891	2.526835	H	-0.016546	-2.364644	-0.661237
C	0.764986	-1.936693	2.348836	H	-1.737424	-1.945698	-0.181410

S=(H)P-Mo(CO)$_5$ E = -1372.989870000 au

ZPE = 0.052221590 au

G_{corr} = 0.00783457 au

P	0.548823	0.981127	0.078932	O	3.190487	1.155207	2.935836
H	1.876998	1.270938	-0.342498	C	-0.534138	2.188533	2.813715
S	-0.600988	1.297432	-1.431824	O	-0.930529	3.222512	3.074285
Mo	0.171249	0.293859	2.345663	C	-1.745569	-0.256251	1.794834
C	-0.124836	-0.247508	4.313067	O	-2.790457	-0.559990	1.464143
O	-0.283452	-0.538836	5.402808	C	0.819764	-1.634473	1.944143
C	2.107660	0.849688	2.748796	O	1.168155	-2.697422	1.734149

TS(**VIb** inverse retro [2+2]) E = -1451.355735738 au

ZPE = 0.103662730 au

G_{corr} = 0.05657499 au

$\bar{\upsilon}$ = -376.16 cm^{-1}

Mo	0.063341	-0.119715	2.576023	O	1.520961	-2.963409	2.764391
C	0.347151	0.187767	4.569508	P	-0.235653	-0.499234	0.156396
O	0.510738	0.367182	5.686323	H	0.938971	-0.293975	-0.624649
C	1.852827	0.791923	2.138698	S	-1.428327	0.791932	-1.134375
O	2.845907	1.287336	1.868480	C	-0.865719	-0.021881	-2.483592
C	-0.922483	1.685005	2.431635	H	-1.465376	-0.016563	-3.384940
O	-1.479800	2.677146	2.340041	H	0.160561	-0.354921	-2.543025
C	-1.728605	-1.069061	2.931017	C	-1.076555	-1.879658	-0.521198
O	-2.715615	-1.609502	3.120700	H	-1.000877	-2.828914	0.000718
C	1.009502	-1.944425	2.697896	H	-1.948961	-1.741545	-1.131862

H_2C=P(H)-Mo(CO)$_5$ E = -1014.461354622 au

ZPE = 0.076548290 au

G_{corr} = 0.03249052 au

Mo	0.005566	-0.423678	2.479063	O	-1.995650	-2.393487	4.027230
C	0.322613	0.602625	4.201991	C	1.585966	-1.672440	2.905009
O	0.506032	1.187543	5.166375	O	2.464395	-2.365595	3.129414
C	1.299606	0.875006	1.529335	P	-0.386615	-1.670023	0.390947
O	2.020778	1.604231	1.030999	H	0.443157	-2.713345	-0.077155
C	-1.575502	0.800622	1.990626	C	-1.562760	-1.593461	-0.764618
O	-2.452623	1.473114	1.705699	H	-2.363523	-0.870525	-0.678031
C	-1.285054	-1.695324	3.472753	H	-1.577914	-2.245023	-1.627279

TS(**VIb**→**VIIb**) E = -1451.423737748 au

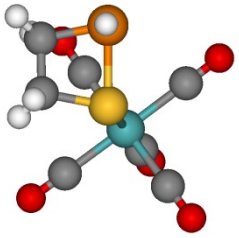
ZPE = 0.10773739 au

G_{corr} = 0.06074103 au

$\bar{\upsilon}$ = -162.09 cm^{-1}

Mo	-0.132356	-0.050822	0.276285	O	2.214062	2.099497	-0.040649
C	0.091469	-0.059231	2.215319	C	-1.479801	1.481238	0.498931
O	0.219964	-0.064194	3.359061	O	-2.217608	2.339570	0.659667
C	1.262101	-1.572185	0.141993	C	-1.664928	-1.424582	0.451030
O	2.052495	-2.394243	0.123262	O	-2.518060	-2.170854	0.581601
C	1.378942	1.327892	0.073209	P	-1.258371	0.267710	-2.619132

H	-1.738525	-0.135862	-3.900863	H	0.704598	1.410357	-4.756540
S	0.847560	-0.149991	-2.899768	C	-0.630304	1.965377	-3.105946
C	0.727302	1.532011	-3.673989	H	-1.266348	2.511623	-3.800675
H	1.569095	2.163759	-3.396039	H	-0.516241	2.554011	-2.197178



VIIb E = -1451.453132525 au

ZPE = 0.10881037 au

G_{corr} = 0.06223437 au

Mo	-0.264625	-0.094498	0.111804	O	-0.139358	2.719730	1.639225
C	1.679732	0.059396	-0.318174	P	-3.779630	1.490063	0.230854
O	2.795814	0.147209	-0.568786	H	-4.988184	1.156267	0.908276
C	0.234843	-1.085716	1.856587	S	-2.744262	-0.365029	0.800395
O	0.540629	-1.630795	2.810938	C	-3.773996	-0.945393	-0.638841
C	-0.341973	-1.884441	-0.894724	H	-3.220585	-1.638251	-1.268257
O	-0.383156	-2.875064	-1.464297	H	-4.650973	-1.442815	-0.226894
C	-0.700258	0.905850	-1.620458	C	-4.115612	0.407032	-1.267551
O	-0.910969	1.473484	-2.592168	H	-5.127691	0.484301	-1.662414
C	-0.193164	1.714228	1.102224	H	-3.414343	0.676959	-2.054206

VIc E = -1450.314369963 au

ZPE = 0.109125061 au

G_{corr} = 0.06167190 au

W	0.074322	-0.040398	2.557151	O	1.264020	-3.017956	2.684251
C	0.093721	0.055373	4.600803	P	0.034316	-0.204711	0.086732
O	0.103563	0.103649	5.744161	H	1.272841	-0.131703	-0.597136
C	1.992331	0.723009	2.448628	S	-1.206548	0.993002	-1.180158
O	3.053169	1.139502	2.359250	C	-1.239019	-0.643376	-2.058907
C	-0.704317	1.878333	2.447461	H	-2.230004	-0.861712	-2.451312
O	-1.137741	2.931846	2.371558	H	-0.519190	-0.630751	-2.876033
C	-1.840235	-0.809993	2.553785	C	-0.786077	-1.543656	-0.898159
O	-2.897813	-1.245137	2.520456	H	-0.148990	-2.384403	-1.170856
C	0.841494	-1.955515	2.642395	H	-1.637854	-1.909916	-0.325884

TS(**VIc→VIIc**) E = -1450.262573904 au

ZPE = 0.10770633 au

G_{corr} = 0.06046700 au

$\bar{\upsilon}$ = -174.63 cm^{-1}

Cr	-0.120175	-0.046076	0.299669	O	-0.716990	-2.432324	-1.648045
W	-0.219575	0.231082	0.066470	C	-0.480998	1.362999	-1.634358
C	1.705980	0.202286	-0.319512	O	-0.593917	1.990263	-2.585426
O	2.835503	0.184844	-0.550181	C	-0.002231	1.961646	1.181741
C	0.139202	-0.908948	1.761343	O	0.137413	2.919896	1.788265
O	0.392139	-1.541786	2.678130	P	-3.235818	0.985141	0.165331
C	-0.523671	-1.485810	-1.033981	H	-4.466610	1.416829	0.744433

S	-3.146333	-1.016267	0.985140	C	-3.946158	-0.000706	-1.261852
C	-4.214685	-1.308185	-0.504159	H	-4.820863	0.441888	-1.735598
H	-3.925791	-2.215405	-1.031613	H	-3.165522	-0.121722	-2.010858
H	-5.248835	-1.393206	-0.171737				

VIIc E = -1450.296282412 au

ZPE = 0.10873862 au

G_{corr} = 0.06180710 au

W	-0.259354	-0.099653	0.109747	O	-0.157781	2.731171	1.626852
C	1.699168	0.056121	-0.316636	P	-3.789854	1.485674	0.256764
O	2.817539	0.145322	-0.563789	H	-4.988300	1.125775	0.938438
C	0.234038	-1.080793	1.869283	S	-2.735742	-0.375973	0.789397
O	0.531895	-1.619596	2.831662	C	-3.767665	-0.934771	-0.659290
C	-0.335238	-1.904341	-0.886745	H	-3.209910	-1.609585	-1.304221
O	-0.378708	-2.901412	-1.448227	H	-4.636954	-1.448979	-0.251847
C	-0.702182	0.888214	-1.637641	C	-4.124655	0.426650	-1.258581
O	-0.923243	1.446407	-2.614765	H	-5.139984	0.502248	-1.645265
C	-0.199689	1.721631	1.092808	H	-3.431141	0.718405	-2.044413

VIIIa (or **Xa**) E = -459.802712533862 au (B3LYP-D3/def2-TZVPP)

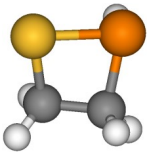
P	-0.027470	-0.112118	-0.158980	H	2.469564	-0.489733	-0.713830
C	1.850426	0.011085	0.027744	H	2.487791	2.086930	0.610276
C	1.777336	1.551989	-0.026441	H	1.919259	1.895810	-1.052785
C	0.290792	1.675289	0.369213	H	0.158112	1.750831	1.449842
H	-0.031110	0.170862	-1.554672	H	-0.293650	2.458093	-0.110326
H	2.128827	-0.352654	1.018502				

VIIIb E = -475.844771441430 au (B3LYP-D3/def2-TZVPP)

N	-0.029854	-0.003139	-0.115522	H	2.109402	-0.192492	-1.236466
P	1.705138	0.022509	0.116976	H	1.482316	2.396366	0.883459
C	1.317331	1.856250	-0.048265	H	1.801514	2.391723	-0.861572
C	-0.164513	1.464916	-0.285598	H	-0.858924	1.919698	0.424324
H	-0.570286	-0.410292	0.633686	H	-0.506904	1.710629	-1.295070

VIIIc E = -574.365779826434 au (B3LYP-D3/def2-TZVPP)

O	0.043777	0.007594	0.007056	H	1.513771	2.264411	-1.075087
P	1.704923	0.117656	0.117932	H	1.413471	2.360344	1.990917
C	1.862644	1.957532	-0.086658	H	1.101150	3.717052	0.923168
C	1.017117	2.630710	1.005760	H	-1.026745	2.705941	1.722349
C	-0.457887	2.218413	0.925477	H	-0.881124	2.553358	-0.026268
C	-0.651907	0.710327	1.041155	H	-0.308302	0.359626	2.024358
H	1.955077	-0.250579	-1.231604	H	-1.703165	0.441274	0.934558
H	2.915154	2.237211	0.007279				



VIIId E = -818.681732617439 au (B3LYP-D3/def2-TZVPP)

E = -817.698809793820 au

ZPE = 0.06635142 au

G_{corr} = 0.039385441 au

P	-0.825343	0.147701	-0.729040	H	-1.606677	-2.012516	0.110545
H	-0.962738	1.311067	0.088956	C	-0.165607	-1.060024	1.436938
S	1.039157	-0.555946	0.121771	H	0.094402	-2.018144	1.886464
C	-1.440368	-1.045447	0.586152	H	-0.189866	-0.291757	2.210687
H	-2.349519	-0.744403	1.107351				

TS(**VIIId** normal retro [2+2]) E = -817.698809793820 au

ZPE = 0.06635142 au

G_{corr} = 0.039385441 au

$\bar{\upsilon}$ = -448.50 cm^{-1}

P	-0.588344	-0.008992	-0.526668	H	-1.805363	-2.144444	0.266579
H	-0.896954	1.129942	0.284226	C	-0.433708	-1.049039	1.499657
S	1.433865	-0.338535	-0.188101	H	0.283460	-1.846805	1.567322
C	-1.607803	-1.187387	0.732909	H	-0.315434	-0.231265	2.195475
H	-2.476279	-0.592945	0.988425				

$H_2C{=}CH_2$ E = -78.439324272 au

ZPE = 0.050917810 au

G_{corr} = 0.02978132 au

C	-1.846400	-2.156783	1.508935	C	-1.238354	-0.994229	1.693590
H	-1.348470	-3.098321	1.708332	H	-0.217863	-0.935398	2.053144
H	-2.866890	-2.215547	1.149366	H	-1.736343	-0.052722	1.494187

H-P=S E = -739.217079473 au

ZPE = 0.008698850 au

G_{corr} = -0.01448014 au

H	1.911873	1.711411	-0.383367	S	0.296519	-0.192193	-1.249610
P	0.646599	1.701096	-1.075882				

TS(**VIIId** inverse retro [2+2]) E = -817.586063528 au

ZPE = 0.060316720 au

G_{corr} = 0.03309250 au

$\bar{\upsilon}$ = -344.24 cm^{-1}

P	-0.936454	0.295652	-0.462438	H	-1.644627	-1.936601	0.369436
H	-0.636348	1.164975	0.650635	C	0.379496	-1.051365	1.601773
S	0.719670	-0.997046	-0.048050	H	0.921692	-1.767626	2.208438
C	-1.998298	-0.925374	0.266649	H	-0.137652	-0.237997	2.083109
H	-3.074040	-0.814089	0.150273				

H_2C=S E = -436.929943543 au

ZPE = 0.024643030 au

G_{corr} = 0.00271185 au

S	0.977760	-2.904119	1.108158	H	0.457338	-0.849751	2.176136
C	0.895304	-1.311060	1.292109	H	1.273201	-0.618582	0.541214

H_2C=PH E = -380.698210963 au

ZPE = 0.033503230 au

G_{corr} = -381.173132570 au

P	-1.971882	1.099872	0.259239	H	-1.369008	-0.923144	-0.857926
H	-2.631103	1.075141	1.524737	H	-2.196118	-1.294897	0.735080
C	-1.842051	-0.542930	0.041079				

IXa E = -420.496613617215 au (B3LYP-D3/def2-TZVPP)

H	0.000397	0.002538	-0.001271	H	0.752532	2.447062	0.301323
P	1.421103	-0.000127	0.000023	H	2.550149	2.219860	0.391683
C	1.607617	1.857491	0.000251	H	0.752384	1.436218	-2.003912
C	1.607492	1.258254	-1.366360	H	2.550092	1.215832	-1.897903

IXb E = -436.534422635160 au (B3LYP-D3/def2-TZVPP)

N	1.388867	1.909772	-0.030162	C	1.596060	1.289963	-1.333065
H	2.250154	2.292588	0.348060	H	0.770495	1.412697	-2.023854
P	1.425568	0.129503	0.074311	H	2.579046	1.345679	-1.790216
H	0.014816	-0.050302	0.012447				

IXc E = -456.412990369119 au (B3LYP-D3/def2-TZVPP)

O	0.004156	0.003639	-0.000495	H	1.928442	-0.019318	1.413944
P	1.700745	-0.004182	-0.000945	H	0.301458	1.896772	0.911990
C	0.496093	1.343762	-0.001889	H	0.328011	1.888437	-0.926094

IXd E = -779.377596215434 au (B3LYP-D3/def2-TZVPP)

C	0.028577	0.007553	0.012611	H	1.958924	1.403869	0.562533
S	-0.003797	-0.000377	1.829583	H	-0.314282	-0.908690	-0.452868
P	1.758933	-0.005722	0.641821	H	-0.337896	0.913985	-0.453757

Xb E = -475.831067458572 au (B3LYP-D3/def2-TZVPP)

P	-0.064614	-0.101003	-0.089166	N	-0.934669	1.590755	1.398144
H	1.217716	0.358591	0.315761	H	-1.760414	2.033938	1.787967
C	-0.857854	1.612806	-0.071485	C	-0.857816	0.136073	1.608419
H	-1.831099	1.570233	-0.577470	H	-1.831145	-0.371006	1.631665
H	-0.277804	2.437937	-0.484847	H	-0.277631	-0.167990	2.479789

Xc E = -495.698915594734 au (B3LYP-D3/def2-TZVPP)

P	-0.185411	-0.179447	-0.157491	O	-0.951407	1.569058	1.379351
H	1.158466	0.168219	0.147098	C	-0.837293	0.150756	1.583917
C	-0.837436	1.589851	-0.053548	H	-1.818763	-0.308010	1.745204
H	-1.818612	1.691572	-0.529789	H	-0.181386	-0.088219	2.420484
H	-0.181211	2.388667	-0.397973				

Xd E = -818.664984274444 au (B3LYP-D3/def2-TZVPP)

P	-0.254132	-0.067386	-0.061490	S	-0.505332	1.940662	1.767107
H	1.157833	0.038716	0.035708	C	-0.562180	0.104731	1.785597
C	-0.562152	1.787803	-0.062624	H	-1.544428	-0.268886	2.073097
H	-1.544467	2.038724	-0.461623	H	0.195850	-0.345335	2.422219
H	0.195672	2.379527	-0.570574				

XIa E = -461.035648404822 au (B3LYP-D3/def2-TZVPP)

P	1.802488	-0.224846	-0.924510	H	-1.662606	-1.702648	-0.457325
C	2.040432	1.526774	-1.489811	H	-0.133203	-2.169657	0.291465
C	-0.578395	-1.698927	-0.587401	H	-0.345932	-2.325498	-1.451390
H	1.886507	-0.837154	-2.204947	C	-0.053441	-0.276531	-0.780237
H	1.860291	2.197237	-0.647811	H	-0.315658	0.339598	0.084646
H	3.074065	1.666751	-1.808978	H	-0.514229	0.189043	-1.655176
H	1.375042	1.804236	-2.308746				

XIb E = -477.082673289280 au (B3LYP-D3/def2-TZVPP)

P	1.856527	0.134244	-0.190061	H	1.207411	0.719983	-2.529132
C	1.755175	1.184128	-1.708538	H	-1.512574	-1.322173	-0.604128
C	-0.469545	-1.215972	-0.908282	H	-0.024404	-2.217284	-0.982113
H	2.400931	-1.012200	-0.854202	H	-0.463068	-0.773380	-1.904836
H	1.279276	2.131440	-1.453504	N	0.233671	-0.346644	0.024277
H	2.773279	1.391009	-2.046601	H	0.013494	-0.534961	0.989841

XIc E = -496.958718294674 au (B3LYP-D3/def2-TZVPP)

O	0.494024	-0.402017	0.205156	H	3.604805	0.930923	1.375128
P	2.031711	0.042655	-0.236205	H	1.952309	0.970462	2.035957
C	2.663599	0.382530	1.455392	H	-1.179307	-1.447834	-0.277893
C	-0.324323	-1.006279	-0.788839	H	0.216301	-1.787817	-1.332032
H	1.796602	1.414314	-0.576909	H	-0.687400	-0.263592	-1.506922
H	2.855894	-0.560454	1.967339				

XId E = -819.909321220863 au (B3LYP-D3/def2-TZVPP)

S	-0.212428	-0.088077	-0.821052	H	3.334339	1.732629	0.086537
P	1.905009	-0.110331	-0.610498	H	1.726906	2.359309	-0.354556
C	2.258246	1.548411	0.141272	H	-1.740956	-1.500354	0.323352
C	-0.666606	-1.347850	0.420618	H	-0.446596	-1.005590	1.430111
H	2.164753	0.251896	-1.956380	H	-0.150168	-2.284963	0.223572
H	1.969724	1.523595	1.192482				

XII E = -516.038746373485 au (B3LYP-D3/def2-TZVPP)

S	-0.151940	-0.330284	0.042264	H	-0.436182	1.039681	2.113572
C	-0.046601	0.059526	1.847235	H	1.921517	-0.597030	2.681066
C	1.486659	-0.084649	1.820851	H	1.960899	0.892277	1.726976
C	1.565215	-0.853497	0.488530	H	1.624653	-1.934652	0.611608
H	-0.546764	-0.705081	2.441093	H	2.327346	-0.525548	-0.215102

XIII E = -892.869420440428 au

ZPE = 0.07130226 au

G_{corr} = 0.04276545 au

P	0.003390	-0.007647	0.000049	H	-0.187910	-1.888711	-1.468522
H	-0.023121	0.023858	1.413644	C	1.696766	-1.806060	-0.356669
S	2.065854	0.013786	-0.484409	H	2.177080	-2.349210	-1.166562
C	0.155667	-1.772196	-0.440373	H	2.054151	-2.187273	0.597043
H	-0.371201	-2.478953	0.200135	O	-0.973311	0.900777	-0.622480

XIV E = -892.789336612643 au

ZPE = 0.06938296 au

G_{corr} = 0.04069569 au

P	-0.072943	0.006605	0.023582	H	0.243938	-2.054995	-1.245815
H	0.059597	0.011573	1.442387	C	1.848495	-1.727915	0.180896
S	2.198374	0.062643	-0.215036	H	2.538234	-2.358574	-0.381102
C	0.373120	-1.809696	-0.192159	H	2.018924	-1.853229	1.251512
H	-0.223773	-2.504115	0.398426	O	2.498379	0.144404	-1.672231

$Cr(CO)_5$ E = -1609.388452647 au

ZPE = 0.04171680 au

G_{corr} = 0.00300313 au

Cr	0.056507	-0.042065	2.467290	O	-1.090205	2.793566	2.388576
C	0.073371	0.026557	4.314514	C	-1.723645	-0.761007	2.496575
O	0.083123	0.067358	5.460029	O	-2.780326	-1.184745	2.559632
C	1.834886	0.679283	2.405121	C	0.778684	-1.820741	2.514333
O	2.890432	1.110351	2.412913	O	1.208374	-2.874255	2.588983
C	-0.663781	1.736098	2.389091				

$Mo(CO)_5$ E = -633.706485545 au

ZPE = 0.04079191 au

G_{corr} = 0.00104511 au

Mo	0.072715	-0.050053	2.491960	O	-1.121030	2.921671	2.426753
C	0.085708	0.052537	4.433188	C	-1.842672	-0.814250	2.571146
O	0.092959	0.111746	5.580971	O	-2.900579	-1.229279	2.664687
C	1.984814	0.725680	2.460246	C	0.846606	-1.959706	2.614322
O	3.039004	1.158956	2.492948	O	1.274975	-3.009760	2.732703
C	-0.697599	1.863045	2.416395				

$W(CO)_5$ E = -632.542344565 au

ZPE = 0.04076720 au

G_{corr} = 0.00054030 au

W	0.073747	-0.047246	2.521657	O	-1.121864	2.930517	2.410365
C	0.086177	0.052274	4.473545	C	-1.846820	-0.815159	2.574072
O	0.093205	0.109176	5.623380	O	-2.906752	-1.235066	2.638290
C	1.992271	0.725885	2.466123	C	0.846513	-1.964508	2.618021
O	3.050025	1.155978	2.470484	O	1.273348	-3.019757	2.708470
C	-0.697338	1.870617	2.425491				

dppe E = -1685.142842786 au

ZPE = 0.42186056 au

G_{corr} = 0.37385304 au

P	1.371510	0.375228	-0.035495	H	3.841895	-3.740469	1.388294
C	1.442032	0.658333	1.802632	H	2.858389	-1.534257	1.792584
H	2.490269	0.695654	2.106286	C	-0.429088	0.005648	-0.178426
H	0.975749	-0.183792	2.318793	C	-0.994283	-1.206075	0.226304
C	0.747875	1.970432	2.163139	C	-2.367035	-1.401799	0.163780
H	1.350102	2.819265	1.835078	C	-3.199524	-0.384195	-0.292131
H	-0.214381	2.060212	1.658447	C	-2.649952	0.825996	-0.698211
P	0.500359	2.158382	3.999139	C	-1.272447	1.013627	-0.651276
C	2.080313	-1.308402	-0.204473	H	-0.356752	-1.999831	0.593167
C	1.978063	-1.926356	-1.456952	H	-2.789607	-2.347370	0.480001
C	2.520588	-3.182577	-1.679242	H	-4.270543	-0.536611	-0.336285
C	3.196556	-3.842578	-0.656129	H	-3.290571	1.620937	-1.058663
C	3.317603	-3.235729	0.586289	H	-0.844766	1.952716	-0.981517
C	2.760630	-1.979926	0.812499	C	-0.539093	3.677607	3.972860
H	1.459850	-1.417568	-2.261691	C	-1.881549	3.711441	4.353323
H	2.422094	-3.646340	-2.652761	C	-2.598529	4.903357	4.319777
H	3.626904	-4.820572	-0.829615	C	-1.988918	6.078913	3.900993

C	-0.647845	6.060259	3.530248	C	-1.620545	-0.768015	5.910560
C	0.070858	4.874077	3.577419	C	-2.579929	-1.164252	4.986758
H	-2.374976	2.803761	4.671809	C	-2.622447	-0.560877	3.733838
H	-3.639944	4.908591	4.617251	C	-1.715700	0.438245	3.407959
H	-2.550310	7.003945	3.868505	H	0.050204	0.524674	6.293237
H	-0.159625	6.972330	3.209991	H	-1.577966	-1.235500	6.886242
H	1.120262	4.878513	3.305131	H	-3.289311	-1.942380	5.239168
C	-0.744343	0.846339	4.327115	H	-3.360163	-0.867989	3.004120
C	-0.706026	0.225046	5.577489	H	-1.774298	0.896506	2.430453

CO E = -113.157694712963 au

ZPE = 0.00504032 au

G_{corr} = -0.01342344 au

C	0.251432	-4.298698	0.738225	O	0.567740	-3.510812	0.000000

$[Cr(CO)_4(dppe)]$ E = -3181.445623986 au

ZPE = 0.45959479 au

G_{corr} = 0.39565484 au

Cr	-0.256227	-0.414810	0.445425	C	4.824605	2.768557	0.296685
C	-0.023859	-0.725015	2.264514	C	4.097831	2.306548	1.390228
O	0.121742	-0.909399	3.391864	C	3.269362	1.203317	1.259093
C	-0.638916	-2.237636	0.163515	H	3.851254	0.491393	-2.004327
O	-0.882859	-3.352065	0.010702	H	5.289394	2.461613	-1.777167
C	0.091811	1.420202	0.762656	H	5.462743	3.637126	0.396096
O	0.268553	2.527802	0.997783	H	4.167827	2.813975	2.343582
C	-2.068069	-0.043188	0.662653	H	2.693069	0.861993	2.109768
O	-3.186913	0.184227	0.811749	C	-0.526602	1.725623	-2.401712
P	1.999206	-0.877397	-0.042446	C	-1.753368	2.230014	-2.835974
C	2.069100	-1.454466	-1.797470	C	-1.897781	3.582278	-3.122688
H	1.629691	-2.453658	-1.774500	C	-0.820206	4.447645	-2.979504
H	3.097661	-1.566605	-2.144756	C	0.401996	3.955687	-2.535069
C	1.258402	-0.531445	-2.702930	C	0.545886	2.607296	-2.240950
H	1.811786	0.380354	-2.918638	H	-2.599527	1.566962	-2.952947
H	1.042532	-1.012536	-3.655608	H	-2.856050	3.958183	-3.458046
P	-0.348322	-0.022423	-1.885779	H	-0.934003	5.500540	-3.203429
C	2.948627	-2.185883	0.817125	H	1.243521	4.623798	-2.404149
C	4.332432	-2.286679	0.641504	H	1.495179	2.254052	-1.859732
C	5.047089	-3.308111	1.250255	C	-1.611978	-0.854652	-2.920481
C	4.388964	-4.241243	2.045922	C	-2.670460	-1.547667	-2.338053
C	3.016236	-4.144297	2.231659	C	-3.638640	-2.157761	-3.129659
C	2.299543	-3.120119	1.622884	C	-3.558179	-2.081479	-4.512817
H	4.855053	-1.555592	0.038292	C	-2.507899	-1.385957	-5.106551
H	6.118530	-3.373241	1.109002	C	-1.546155	-0.775610	-4.316471
H	4.947211	-5.036112	2.523904	H	-2.747085	-1.610732	-1.264243
H	2.498608	-4.861156	2.855814	H	-4.453965	-2.691871	-2.659318
H	1.234903	-3.048981	1.782762	H	-4.310410	-2.557366	-5.128964
C	3.159573	0.533963	0.036711	H	-2.442088	-1.316146	-6.184932
C	3.902831	0.995487	-1.049458	H	-0.749073	-0.217181	-4.790601
C	4.725485	2.110959	-0.922010				

$[Mo(CO)_4(dppe)]$ E = -2205.762996306 au

ZPE = 0.45799190 au

G_{corr} = 0.39442829 au

Mo	-0.353294	-0.414925	0.581598	C	4.837083	2.779560	0.217689
C	-0.098436	-0.766247	2.540377	C	4.064596	2.386860	1.306609
O	0.071388	-0.969467	3.660429	C	3.240404	1.276320	1.210409
C	-0.763057	-2.387009	0.274490	H	3.953981	0.363509	-1.976217
O	-1.001678	-3.499497	0.112984	H	5.385863	2.344551	-1.812603
C	0.007093	1.571053	0.933580	H	5.471252	3.653851	0.288477
O	0.184211	2.679345	1.160540	H	4.094690	2.953793	2.227978
C	-2.312417	-0.029987	0.801914	H	2.625979	0.988702	2.053866
O	-3.436876	0.186203	0.915407	C	-0.539929	1.755627	-2.411242
P	2.031171	-0.891603	-0.005600	C	-1.729953	2.259861	-2.936947
C	2.032249	-1.453016	-1.768414	C	-1.854249	3.613951	-3.226095
H	1.553198	-2.433889	-1.745555	C	-0.792433	4.479706	-2.995684
H	3.048216	-1.604947	-2.138004	C	0.393108	3.986965	-2.460805
C	1.251660	-0.491322	-2.660135	C	0.516135	2.637544	-2.162966
H	1.817508	0.424627	-2.819389	H	-2.563100	1.596022	-3.122617
H	1.072687	-0.934585	-3.638905	H	-2.784351	3.990555	-3.632495
P	-0.384288	0.005235	-1.897684	H	-0.890454	5.533622	-3.222206
C	3.007244	-2.208586	0.805455	H	1.221189	4.655440	-2.263232
C	4.380416	-2.330525	0.572928	H	1.434613	2.281330	-1.714130
C	5.102019	-3.363764	1.153015	C	-1.613453	-0.839023	-2.959536
C	4.460827	-4.286343	1.974700	C	-2.682397	-1.522017	-2.383856
C	3.098585	-4.166723	2.217588	C	-3.630721	-2.153798	-3.182109
C	2.375129	-3.129915	1.638879	C	-3.518697	-2.108640	-4.564756
H	4.889737	-1.607962	-0.051761	C	-2.457902	-1.422842	-5.151196
H	6.165701	-3.446863	0.968905	C	-1.515335	-0.790899	-4.354530
H	5.024904	-5.090937	2.428954	H	-2.775982	-1.558064	-1.309100
H	2.595852	-4.875512	2.862761	H	-4.454437	-2.680847	-2.718474
H	1.318515	-3.033517	1.840507	H	-4.254794	-2.602029	-5.186607
C	3.180729	0.531175	0.029296	H	-2.368545	-1.378290	-6.229223
C	3.969464	0.924662	-1.052214	H	-0.708627	-0.241875	-4.823402
C	4.787610	2.046514	-0.960877				

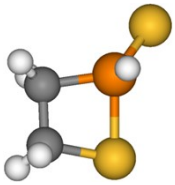
$[W(CO)_4(dppe)]$ E = -2204.608376516 au

ZPE = 0.45781333 au

G_{corr} = 0.39384328 au

W	-0.357677	-0.414541	0.585455	C	3.180928	0.530398	0.028935
C	-0.096891	-0.764944	2.555397	C	3.965108	0.928257	-1.054232
O	0.082136	-0.969421	3.675784	C	4.781204	2.051568	-0.962347
C	-0.766126	-2.397032	0.276942	C	4.832984	2.781224	0.218160
O	-0.998455	-3.512043	0.110504	C	4.065106	2.383750	1.308624
C	0.009739	1.579336	0.931592	C	3.243042	1.271717	1.212317
O	0.196021	2.690348	1.146629	H	3.947845	0.369636	-1.979703
C	-2.328109	-0.024262	0.796489	H	5.375998	2.353309	-1.815182
O	-3.455607	0.193365	0.895767	H	5.465548	3.656643	0.289355
P	2.033897	-0.894124	-0.008832	H	4.097255	2.947983	2.231552
C	2.035721	-1.456074	-1.771371	H	2.632572	0.980054	2.057261
H	1.560967	-2.438991	-1.747708	C	-0.537704	1.752743	-2.411769
H	3.052678	-1.603734	-2.139646	C	-1.730176	2.258705	-2.930101
C	1.252256	-0.498258	-2.664745	C	-1.854512	3.613440	-3.215744
H	1.817275	0.417155	-2.829932	C	-0.790561	4.477582	-2.988850
H	1.070173	-0.946237	-3.640716	C	0.397278	3.982809	-2.461190
P	-0.383048	0.001341	-1.902357	C	0.520746	2.632616	-2.167112
C	3.007293	-2.210297	0.806064	H	-2.564950	1.595971	-3.112254
C	4.379545	-2.333848	0.569264	H	-2.786370	3.991931	-3.616279
C	5.102637	-3.364233	1.152474	H	-0.888843	5.532127	-3.212325
C	4.463756	-4.281674	1.981665	H	1.226782	4.650218	-2.266103
C	3.102407	-4.160070	2.228624	H	1.440878	2.274610	-1.723276
C	2.377178	-3.126416	1.646574	C	-1.614714	-0.840858	-2.962677
H	4.887072	-1.614662	-0.060792	C	-2.683159	-1.525648	-2.388357
H	6.165622	-3.448890	0.965169	C	-3.632078	-2.153958	-3.188534
H	5.029004	-5.083930	2.438575	C	-3.521306	-2.103110	-4.571103
H	2.601622	-4.864851	2.879631	C	-2.460822	-1.415407	-5.155845
H	1.321242	-3.028678	1.851201	C	-1.517315	-0.787102	-4.357461

H	-2.776259	-1.565664	-1.313654	H	-2.372479	-1.366448	-6.233753
H	-4.455646	-2.682435	-2.726308	H	-0.710811	-0.236360	-4.824729
H	-4.258293	-2.593519	-5.194244				



XV E = -1215.462409903 au

ZPE = 0.069366340 au

G_{corr} = 0.03976758 au

P	-0.119519	-0.068736	0.057007	H	-1.866326	-0.702319	-1.459894
H	1.233580	0.197993	-0.244472	C	-1.167173	1.355918	-1.732757
S	-1.013468	1.869708	0.046672	H	-2.146571	1.619591	-2.124695
C	-0.930002	-0.160079	-1.588054	H	-0.396518	1.843285	-2.325985
H	-0.343148	-0.630009	-2.376615	S	-0.366865	-1.369000	1.449769

TS(**XV** normal retro [2+2]) E = -1215.393584238 au

ZPE = 0.066589500 au

G_{corr} = 0.03665450 au

$\tilde{\upsilon}$ = -424.01 cm^{-1}

P	-0.118052	0.248875	0.108275	C	-1.207829	1.108584	-2.027645
H	1.104941	0.378346	-0.575634	H	-2.122206	1.657740	-1.874166
S	-0.819889	2.045247	0.534269	H	-0.401050	1.640994	-2.513344
C	-1.089769	-0.239158	-1.687538	S	-0.149913	-1.271300	1.289382
H	-0.329394	-0.841799	-2.168432	H	-0.016546	-2.364644	-0.661237
H	-1.982850	-0.771178	-1.384188	H	-1.737424	-1.945698	-0.181410

S=(H)P=S E = -1136.985769339 au

ZPE = 0.012601420 au

G_{corr} = -0.01372617 au

H	0.978569	0.536467	-0.590203	S	-0.923913	1.989286	0.815436
P	0.012348	0.376301	0.421764	S	-0.069692	-1.406210	1.091919

TS(**XV** inverse retro [2+2]) E = -1215.347323587 au

ZPE = 0.063842810 au

G_{corr} = 0.03398977 au

$\tilde{\upsilon}$ = -294.03 cm^{-1}

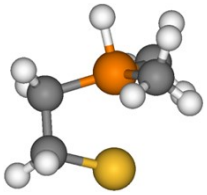
P	-0.112993	-0.174111	-0.147004	H	-1.822378	-0.432143	-1.892810
H	0.904017	0.738800	-0.494598	C	-1.181516	1.960028	-1.584745
S	-1.688333	1.475624	-0.087500	H	-1.900645	2.318083	-2.310738
C	-0.890934	-0.831634	-1.538128	H	-0.129922	2.038501	-1.831280
H	-0.681805	-1.871031	-1.768041	S	0.388499	-1.265767	1.355822

$H_2C=P(H)=S$ E = -778.445353507 au

ZPE = 0.036259030 au

G_{corr} = 0.01065223 au

P	-0.006402	-0.002116	-0.024461	H	-1.581814	1.795796	-0.007108
H	1.397345	0.002647	0.007219	H	0.200227	2.345546	0.048190
C	-0.530622	1.550004	0.008777	S	-0.920490	-1.684624	-0.094627



XVI E = -897.366459956 au

ZPE = 0.142260870 au

G_{corr} = 0.10993898 au

P	0.076630	-0.044791	0.016988	C	-0.071671	-0.917209	-1.574764
S	2.519187	-0.024540	-0.070318	H	-1.103080	-1.221555	-1.757212
C	0.588561	1.723918	-0.002851	H	0.254934	-0.243922	-2.367222
H	-0.117247	2.330433	-0.580522	H	0.597257	-1.774220	-1.572797
H	0.535576	2.054003	1.038314	C	0.079215	-1.161531	1.458471
C	2.030524	1.677465	-0.504948	H	-0.900121	-1.628238	1.578228
H	2.666552	2.419870	-0.023195	H	0.864301	-1.905308	1.340831
H	2.077175	1.840905	-1.582989	H	0.307430	-0.567971	2.344155
H	-1.330628	0.272974	0.146442				

XVI' E = -897.359868696 au

ZPE = 0.142014770 au

G_{corr} = 0.11009250 au

P	0.010384	0.057946	0.073045	C	-0.928579	-0.195032	-1.467812
S	2.123879	0.275919	-1.190429	H	-1.992503	-0.336414	-1.273340
C	0.684386	1.737829	0.418290	H	-0.776525	0.676078	-2.103561
H	-0.115497	2.473340	0.555083	H	-0.513041	-1.052431	-1.991533
H	1.215543	1.639931	1.368685	C	-1.408628	0.104945	1.290172
C	1.658875	1.977471	-0.730609	H	-2.112386	0.907022	1.058547
H	2.521075	2.570857	-0.426162	H	-1.945304	-0.845738	1.272110
H	1.169014	2.496821	-1.556837	H	-1.029129	0.262921	2.302271
H	0.541110	-1.130567	0.595233				

TS(**XVI** normal retro [2+2]) E = -897.312975772 au

ZPE = 0.139775360 au

G_{corr} = 0.10786117 au

$\tilde{\upsilon}$ = -562.91 cm^{-1}

P	0.330383	-0.111231	0.330461	C	2.104154	1.941419	-0.411542
S	2.320151	0.042034	0.750715	H	2.520953	2.581913	0.354300
C	0.719821	1.992503	-0.708264	H	2.809646	1.701195	-1.196066
H	0.432624	1.902731	-1.749517	H	-0.623726	0.668024	0.998315
H	0.116778	2.689781	-0.136473	C	-0.260129	-0.679591	-1.304360

H	-0.472187	-1.749173	-1.285449	H	-1.063245	-1.921349	1.202948
H	-1.161328	-0.123802	-1.562024	H	0.601926	-2.492495	0.969444
H	0.503329	-0.468919	-2.048589	H	0.203742	-1.483931	2.368566
C	-0.008300	-1.658826	1.314146				

$Me_2P(H)=S$ E = -818.945343932 au

ZPE = 0.086806180 au

G_{corr} = - 0.05819619 au

P	0.021168	0.025538	-0.114162	C	-0.388894	1.791993	-0.257519
H	-0.170795	-0.206138	1.267144	H	0.167135	2.385236	0.470851
C	1.833757	-0.046174	-0.254058	H	-0.148664	2.124976	-1.267506
H	2.307759	0.623983	0.465690	H	-1.458957	1.915704	-0.096274
H	2.159797	-1.069976	-0.075175	S	-0.967006	-1.159998	-1.292117
H	2.118264	0.237640	-1.267479				

TS(**XVI** inverse retro [2+2]) E = -897.304353559 au

ZPE = 0.134821570 au

G_{corr} = 0.09899655 au

$\bar{\upsilon}$ = -182.25 cm^{-1}

P	-0.660793	0.127272	0.057331	C	-0.332047	-0.669031	-1.534371
S	3.549347	-0.530471	-0.480544	H	-0.703694	-1.694291	-1.530503
C	-0.179376	1.730913	0.047201	H	-0.841920	-0.110411	-2.320216
H	-0.425406	2.317468	-0.829469	H	0.738796	-0.660861	-1.728872
H	-0.192414	2.262941	0.991017	C	0.156035	-0.819397	1.366743
C	3.118752	1.024352	-0.436863	H	-0.276954	-1.818169	1.438525
H	2.358815	1.408191	0.239495	H	1.222878	-0.890694	1.152339
H	3.548599	1.751705	-1.124481	H	0.012602	-0.302262	2.316445
H	-2.018625	-0.296972	0.262835				

$H_2C=PHMe_2$ E = -460.367523320101 au

ZPE = 0.10877324 au

G_{corr} = 0.08051021 au

P	0.004101	0.001994	0.003454	H	-0.266452	2.155411	-1.020628
C	1.668484	0.004422	0.004835	H	-0.377465	0.852539	-2.215884
H	2.178080	0.958137	-0.036446	C	-0.670731	-1.647331	-0.331256
H	2.180665	-0.799493	0.517081	H	-1.759347	-1.635977	-0.260065
H	-0.827929	0.353598	1.128091	H	-0.360122	-1.971893	-1.323483
C	-0.673716	1.162339	-1.214627	H	-0.275626	-2.346620	0.406631
H	-1.761195	1.205684	-1.137851				

$H_2C=PHMe_2$ & $H_2C=S$ E = -897.306182591 au

ZPE = 0.135161020 au

G_{corr} = 0.09836049 au

P	0.004101	0.001994	0.003454	H	2.178080	0.958137	-0.036446
C	1.668484	0.004422	0.004835	H	2.180665	-0.799493	0.517081

H	-0.827929	0.353598	1.128091
C	-0.673716	1.162339	-1.214627
H	-1.761195	1.205684	-1.137851
H	-0.266452	2.155411	-1.020628
H	-0.377465	0.852539	-2.215884
C	-0.670731	-1.647331	-0.331256
H	-1.759347	-1.635977	-0.260065
H	-0.360122	-1.971893	-1.323483
H	-0.275626	-2.346620	0.406631

References:

[1] (a) SHELXS-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) G. M. Sheldrick, SHELXL-97; University of Göttingen, Göttingen, Germany, **1997**.

[2] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, 42.

[4] ORCA - An *ab initio*, DFT and semiempirical SCF-MO package. Written by F. Neese, Max Planck Institute for Bioinorganic Chemistry, D-45470 Mülheim/Ruhr, 2012. Version 3.0.3. Web page: http://www.cec.mpg.de/forum/portal.php. F. Neese, "The ORCA program system", *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

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

[6] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

[7] D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123-141. ECP parameters for Mo and W have been obtained from the Turbomole basis set library at ftp://ftp.chemie.uni-karlsruhe.de/pub/basen/.

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

[9] A. Bergner, M. Dolg, W. Kuchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431−1441.

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