# Supporting Information

# Halogenation of Diphosphorus Complexes

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# 1Experimental Details

## General procedures

All manipulations were carried out under an inert atmosphere of dried nitrogen using standard Schlenk and glove box techniques. Solvents were dried using a MB SPS-800 device of the company MBRAUN. Deuterated solvents were freshly distilled under nitrogen from $CaH_2$ ($CD_2Cl_2$) and from Na/K alloy ($C_6D_6$).
NMR spectra were recorded on a Bruker Advance III 400 MHz NMR spectrometer. Chemical shifts were measured at room temperature and given in ppm; they are referenced to TMS for $^1H$ and 85% $H_3PO_4$ for $^{31}P$ as external standard. LIFDI-MS spectra (LIFDI = liquid injection field desorption ionization) were measured on a JEOL AccuTOF GCX. ESI-MS spectra (ESI = Electrospray ionization) were measured on an Agilent Q-TOF 6540 UHD. Elemental Analysis (CHN) was determined using a Vario micro cube instrument. The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44GHz and a rectangular resonator TE102 of the company Magnettech GmbH.
The compound $[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (**1**) was synthesized according to literature procedure.[1]
Phosphorous (V) chlorine was purchased from abcr, Phosphorous (V) bromine (95%) from Alfa Aesar, Iodine from Sigma-Aldrich and they all were used as received without any further purifications.

## Synthesis of $[(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_3(I_3)]$ (2)

$[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (**1**) (20 mg, 0.04 mmol, 1 eq) is dissolved in 10 mL of $CH_2Cl_2$. To this solution, a solution of $I_2$ (0.12 mmol, 30.70 mg, 3 eq) in 20 mL of $CH_2Cl_2$ is added. A change in color from bright orange to dark brown is immediately observed. The solution is stirred for 1 hour, then is filtered over celite and stored at room temperature. After two weeks $[(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_3(I_3)]$ (**2**) crystallized as black crystals, suited for X-ray analysis.

Yield **2**: 14 mg, 0.007 mmol, 18%

Both, the NMR as well as the X-band EPR spectra of isolated **2** are silent, suggesting a paramagnetic complex in triplet spin state (see computational details section)

FD-MS ($CH_2Cl_2$): 829.56 (100%, $[C_{10}H_{10}Mo_2I_4^+]$)]; only a fragment could be detected

EA calculated for $C_{20}H_{20}Mo_4P_3I_9$ (1886.84 g·mol$^{-1}$): C: 12.72, H: 1.07; found [%]: C:12.74, H: 0.94

## Synthesis of $[\{CpMo(CO)_2\}_2(\mu\text{-}PBr_2)_2]$ (3a)

$[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (**1**) (20 mg, 0.04 mmol, 1 eq) is dissolved in 10 mL of $CH_2Cl_2$. To this solution, a solution of $PBr_5$ (34.71 mg, 0.08 mmol, 2 eq) in 10 mL of $CH_2Cl_2$ is added. A change in color from bright orange to dark brown is immediately observed. The solution is stirred for 1 hour. The solvent is removed *in vacuo*. The resulting brown residue is dissolved in 5 mL of $CH_2Cl_2$, layered by 10 mL of hexane and stored at -80°C. After two weeks $[\{CpMo(CO)_2\}_2(\mu\text{-}PBr_2)_2]$ (**3a**) crystallized as black blocks, suited for X-ray analysis.

Yield **3a** 10 mg, 0.012 mmol, 29%

$^1H$-NMR (400 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 5.60 (s, 10 H, $C_5\mathit{H}_5$)

$^{31}P\{^1H\}$-NMR (162 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 200.38 (s, 2 P, $(\mathit{P}Br_2)_2$)

$^{13}C\{^1H\}$-NMR (300 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 98.46 (s, 5 C, $\mathit{C}_5H_5$)

FD-MS ($CH_2Cl_2$): 815.38 (100%, [**3a**$^+$])

EA calculated for $C_{14}H_{10}Br_4Mo_2O_4P_2$ (815.49 g·mol$^{-1}$): C: 20.60, H: 1.24; found [%]: C: 19.78, H: 1.97

ATR (Germanium crystal): $\nu$ [cm$^{-1}$] = 1916, 1970 (CO).

## Synthesis of $[\{CpMo(CO)_2\}(CpMoBr_2)(\mu\text{-}PBr_2)_2]$ (4a)

$[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (**1**) (30 mg, 0.06 mmol, 1 eq) is dissolved in 15 mL of $CH_2Cl_2$. To this solution, a solution of $PBr_5$ (154.98 mg, 0.36 mmol, 6 eq) in 20 mL of $CH_2Cl_2$ is added. A change in color from bright orange to brown is observed, together

with the formation of a light brown precipitate. The solution is stirred for 1 hour, then is filtered over celite and stored at room temperature. After two weeks [{CpMo(CO)$_2$}(CpMoBr$_2$)(μ-PBr$_2$)$_2$] (**4a**) crystallized as black blocks, suited for X-ray analysis.

Yield **4a** 30 mg, 0.033 mmol, 54%

$^1$H-NMR (400 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 5.57 (t, 5 H, $^3J_{P,H}$ = 2.45 Hz, $C_5H_5$), 5.67 (s, 5 H, $C_5H_5$)

$^{31}$P{$^1$H}-NMR (162 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 301.23 (s, 2 P, ($P$Br$_2$)$_2$)

$^{13}$C{$^1$H}-NMR (300 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 97.27 (s, 5 C, $C_5H_5$) 103.40 (s, 5C, $C_5H_5$)

ESI-MS ($CH_3CN$): cation mode: *m/z* = 840.41 (3.72% [M - Br]$^+$)

EA calculated for $C_{12}H_{10}Br_6Mo_2O_2P_2$ (917.34 g·mol$^{-1}$): C: 15.68, H: 1.10; found [%]: C: 14.52, H: 1.38 (due to the high sensitivity of **4a** to moisture and air, it was not possible to obtain an exact elemental analysis, despite several attempts)

ATR (Germanium crystal): ν̃ [cm$^{-1}$] = 2015, 2077 (CO).

## Synthesis of [{CpMo(CO)$_2$}$_2$(μ-PCl$_2$)$_2$] (3b)

[{CpMo(CO)$_2$}$_2$(μ,η$^2$:η$^2$-P$_2$)] (**1**) (20 mg, 0.04 mmol, 1 eq) is dissolved in 10 mL of $CH_2Cl_2$. To this solution, a solution of $PCl_5$ (50 mg, 0.24 mmol, 6 eq) in 15 mL of $CH_2Cl_2$ is added. A change in color from bright orange to brown is observed. The solution is stirred for 10 minutes. With these conditions is possible to observe **3b** via NMR spectroscopy but all attempts to isolate it failed since it is always formed in a mixture with **4b**.

Yield **3b** (calculated via NMR) 21.35%

$^1$H-NMR (400 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 5.56 (s, 10 H, $C_5H_5$)

$^{31}$P{$^1$H}-NMR (162 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 236.29 (s, 2 P, ($P$Cl$_2$)$_2$)

LIFDI-MS (toluene): 637.65 (48%, [**3b**$^+$])

EA All attempts to isolate **3b** failed since it is always formed in a mixture with **4b**, therefore it was not possible to obtain an exact elemental analysis.

IR ($CH_2Cl_2$): ν̃ [cm$^{-1}$] = 1932, 1981 (CO). (these bands are obtained from the solution of the crude reaction mixture and are assigned by comparison with the bands obtained from isolated **4b**).

## Synthesis of [{CpMo(CO)$_2$}(CpMoCl$_2$)(μ-PCl$_2$)$_2$] (4b)

[{CpMo(CO)$_2$}$_2$(μ,η$^2$:η$^2$-P$_2$)] (**1**) (25 mg, 0.05 mmol, 1 eq) is dissolved in 15 mL of $CH_2Cl_2$. To this solution, a solution of $PCl_5$ (62.96 mg, 0.30 mmol, 6 eq) in 15 mL of $CH_2Cl_2$ is added. A change in color from bright orange to brown is observed, followed by the formation of a light brown precipitate. The solution is stirred for 1 hour and then is filtered over celite. The resulting bright yellow solution is stored at room temperature. A few hours later [{CpMo(CO)$_2$}(CpMoCl$_2$)(μ-PCl$_2$)$_2$] (**4b**) crystallized as brown blocks, suitable for X-Ray analysis.

Yield **4b** 30 mg, 0.046 mmol, 92%

$^1$H-NMR (400 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 5.51 (t, 5 H, $^3J_{P,H}$ = 2.25 Hz, $C_5H_5$), 5.63 (s, 5 H, $C_5H_5$)

$^{31}$P{$^1$H}-NMR (162 MHz, $CD_2Cl_2$, 300K): δ [ppm] = 337.13 (s, 2 P, ($P$Cl$_2$)$_2$)

$^{13}$C{$^1$H}-NMR (300 MHz, $C_6D_6$, 300K): δ [ppm] = 101.87 (s, 5 C, $C_5H_5$), 94.33 (s, 5 C, $C_5H_5$)

FD-MS (toluene):653.63 (100%, [**4b**$^+$])

EA calculated for $C_{12}H_{10}Cl_6Mo_2O_2P_2$ (653.64 g·mol$^{-1}$): C: 22.03, H: 1.54; found [%]: C:22.14, H: 1.84

IR ($CH_2Cl_2$): ν̃ [cm$^{-1}$] = 2030, 2059 (CO).

# 2Selected NMR

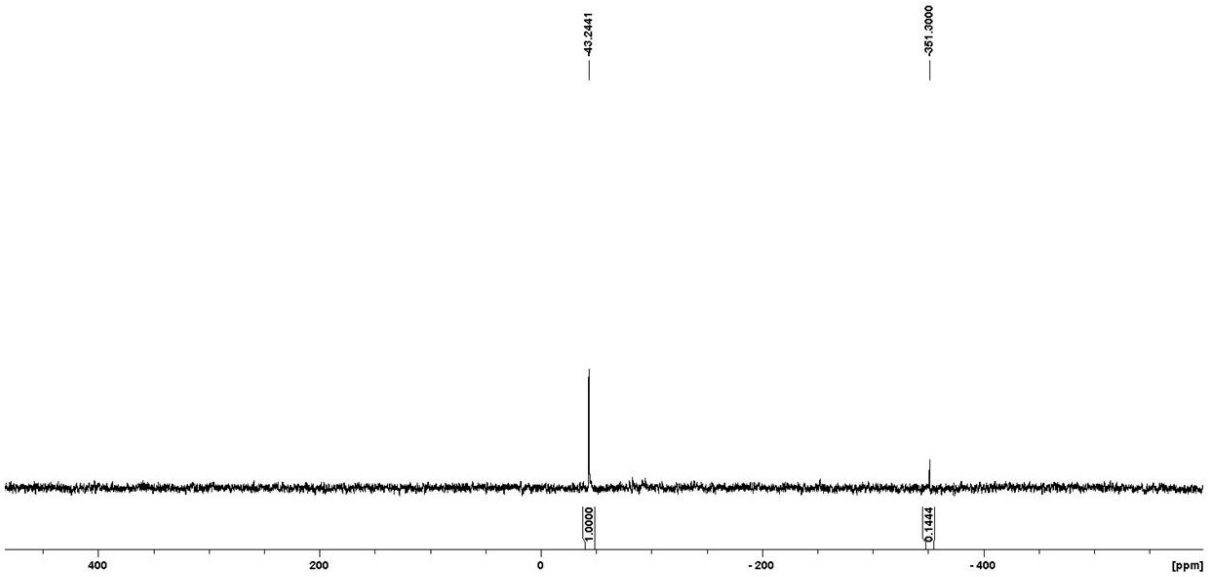


**Figure S 1** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $I_2$ (1 eq) ($C_6D_6$ capillary, 300K)

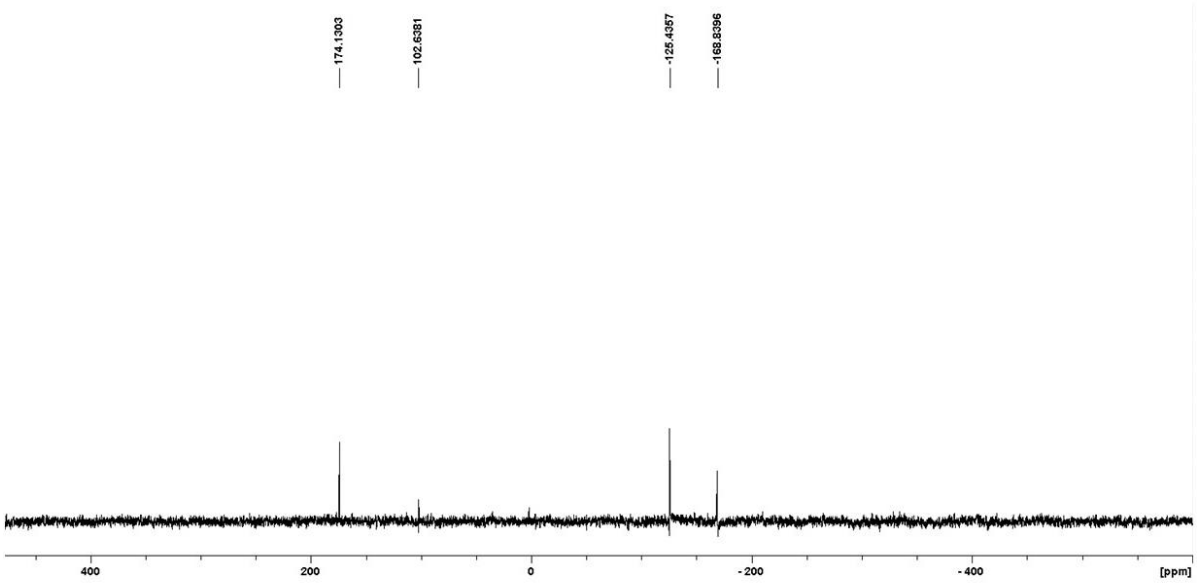


**Figure S 2** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $I_2$ (3 eq) ($C_6D_6$ capillary, 300K)

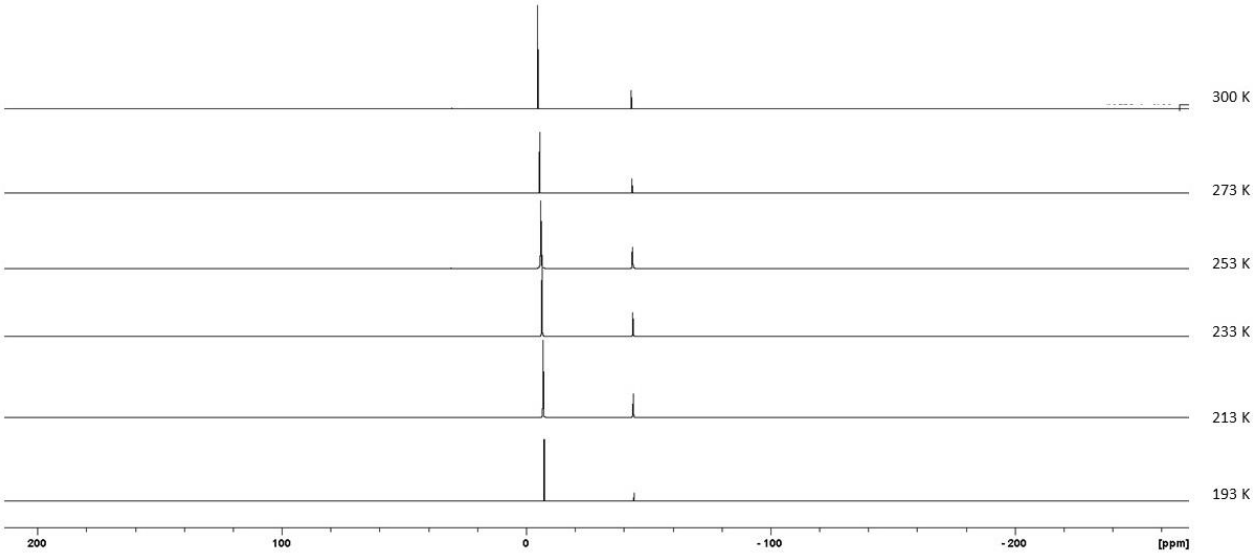


**Figure S 3** VT $^{31}P\{^{1}H\}$ NMR spectra of the solution of the reaction between **1** (1eq) and $I_2$ (3 eq) ($CD_2Cl_2$ and $PPh_3$ as a reference δ =-4.9 ppm).

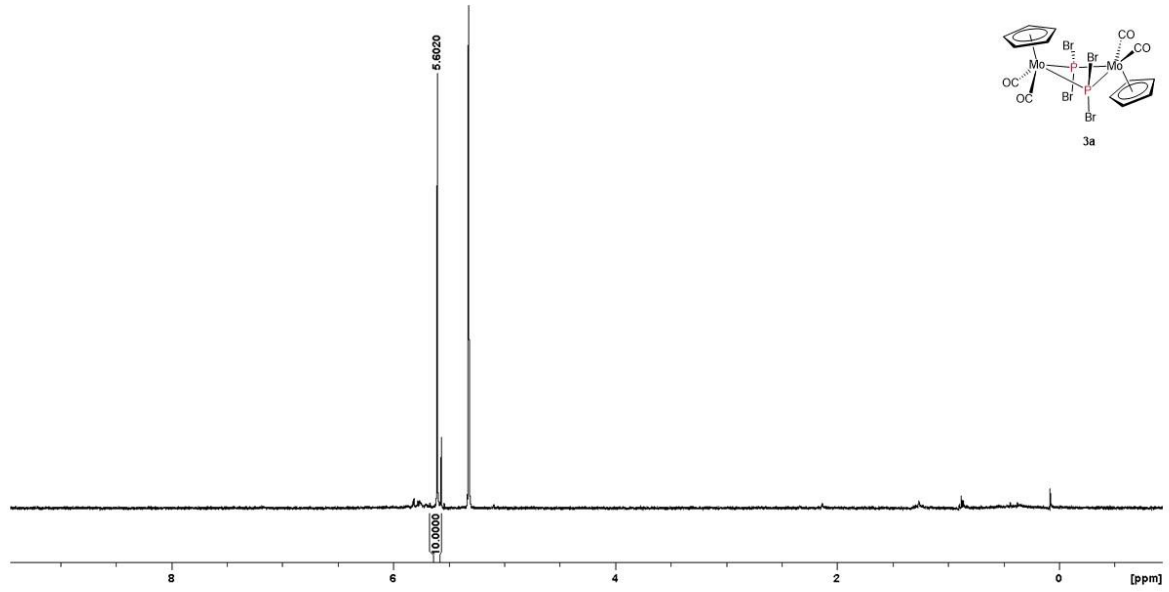


**Figure S 4** $^{1}H$ NMR spectrum of compound **3a** ($CD_2Cl_2$, 300 K)

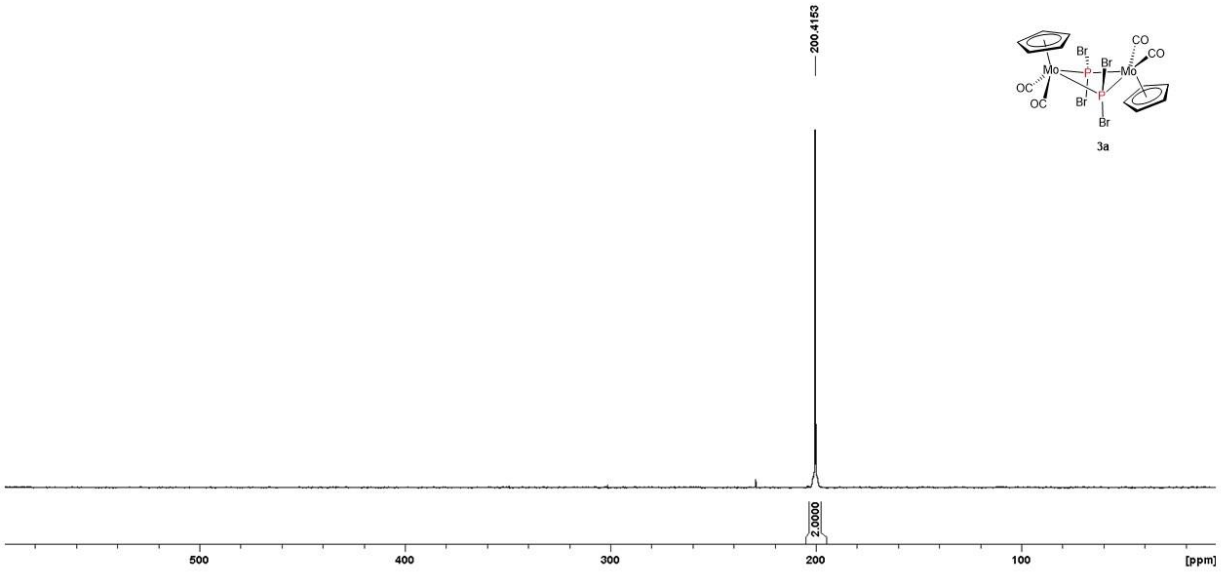


**Figure S 5** $^{31}P\{^{1}H\}$ NMR spectrum of compound **3a** ($CD_2Cl_2$, 300 K)

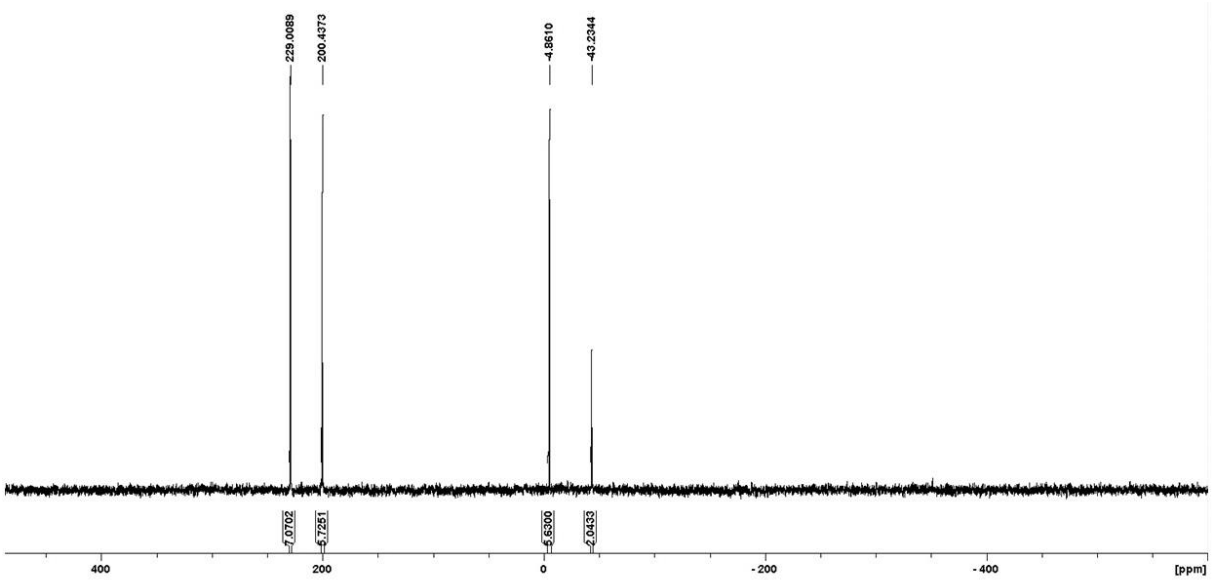


**Figure S 6** $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution of **1** (1 eq) with $PBr_5$ (1 eq) and $PPh_3$ as a reference ($C_6D_6$ capillary, 300 K)

- mmol $PPh_3$ in the inner part of the Evans NMR tube: $8.0 \cdot 10^{-4}$
- mmol $PBr_5$ in the external part of the Evans NMR tube: $4.5 \cdot 10^{-3}$

- $\frac{PBr_5}{PPh_3} = \frac{4.5 \cdot 10^{-3}}{8.0 \cdot 10^{-4}} = 5.63$
- Integration $PPh_3 = 5.63$
- Integration $PBr_3 = 7.07$
- 5.63 out of 7.07 (**80%**) equals the amount of $PBr_3$ coming from $PBr_5$
- (7.07 – 5.63) = 1.44 (**20%**) equals the amount of $PBr_3$ coming from **1**

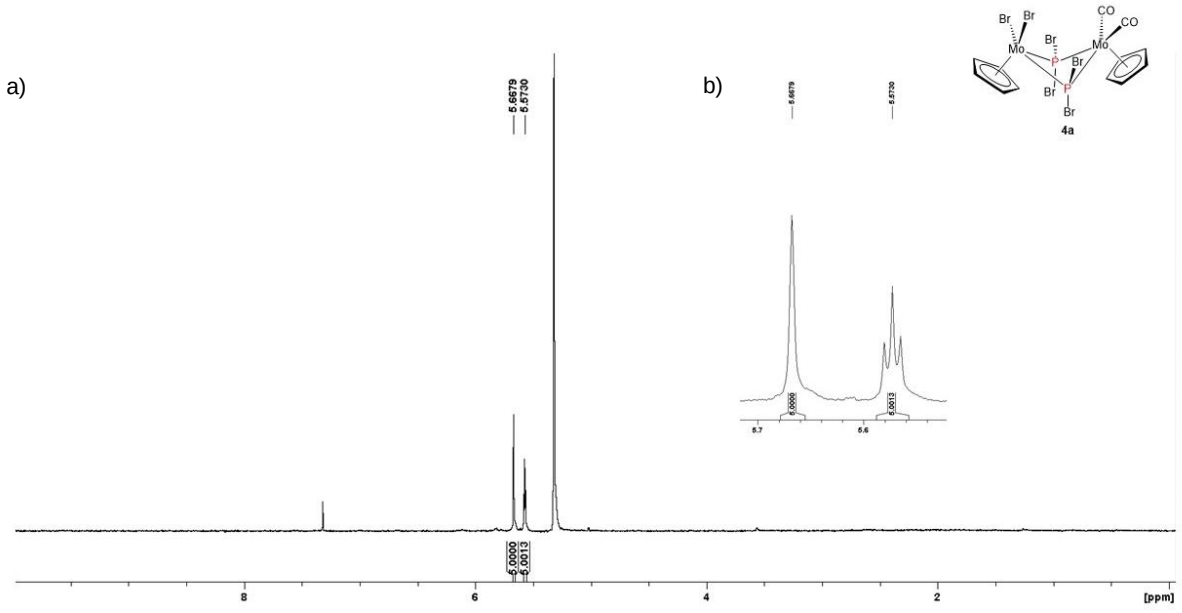


**Figure S 7** $^{1}H$ NMR spectrum of compound **4a** (a) ($CD_2Cl_2$, 300 K) and zoom on the signals (b)

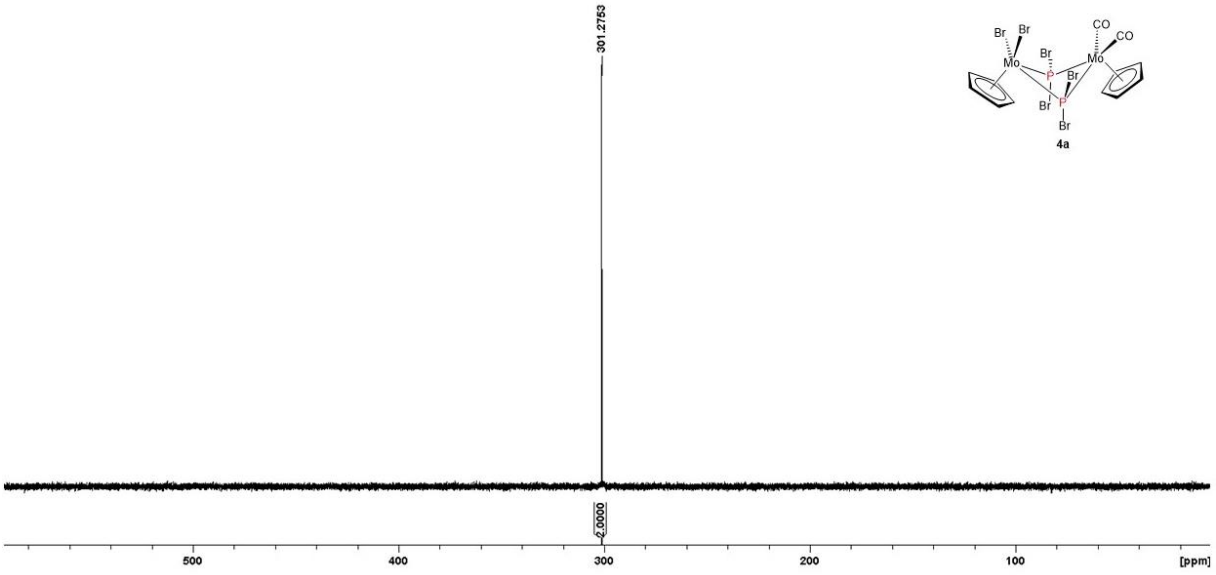


**Figure S 8** $^{31}P\{^{1}H\}$ NMR spectrum of compound **4a** ($CD_2Cl_2$, 300 K)

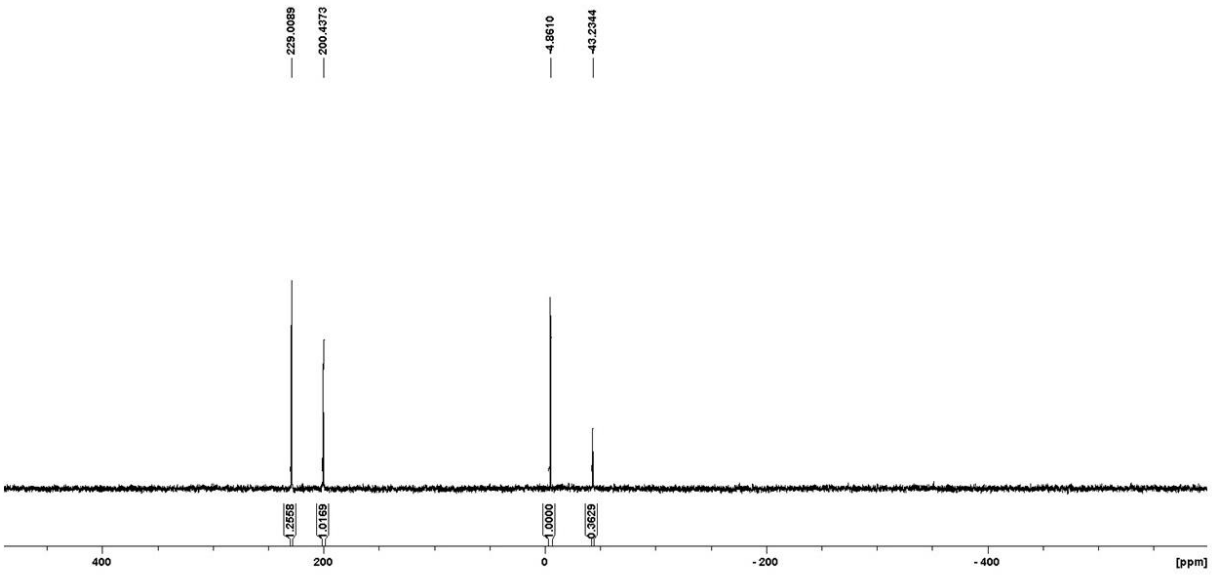


**Figure S 9** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (1 eq) ($C_6D_6$ capillary and $PPh_3$ as a reference δ =-4.9 ppm, 300K)

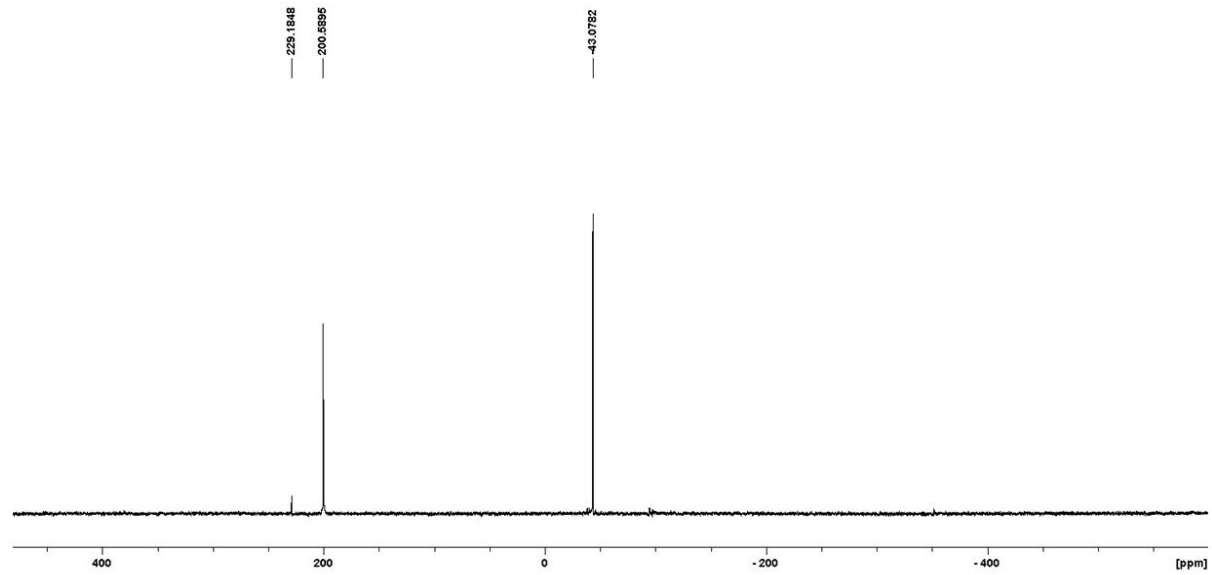


**Figure S 10** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1eq) and $PBr_5$ (2 eq) after seven hours ($C_6D_6$ capillary, 300K)

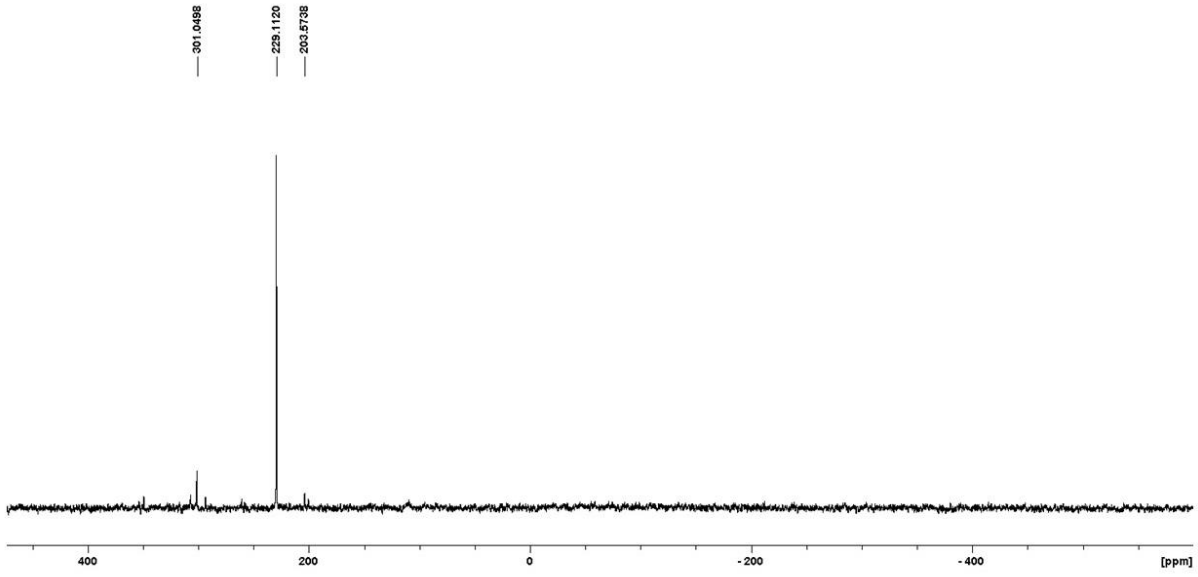


**Figure S 11** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (2 eq) after seven days ($C_6D_6$ capillary, 300K)

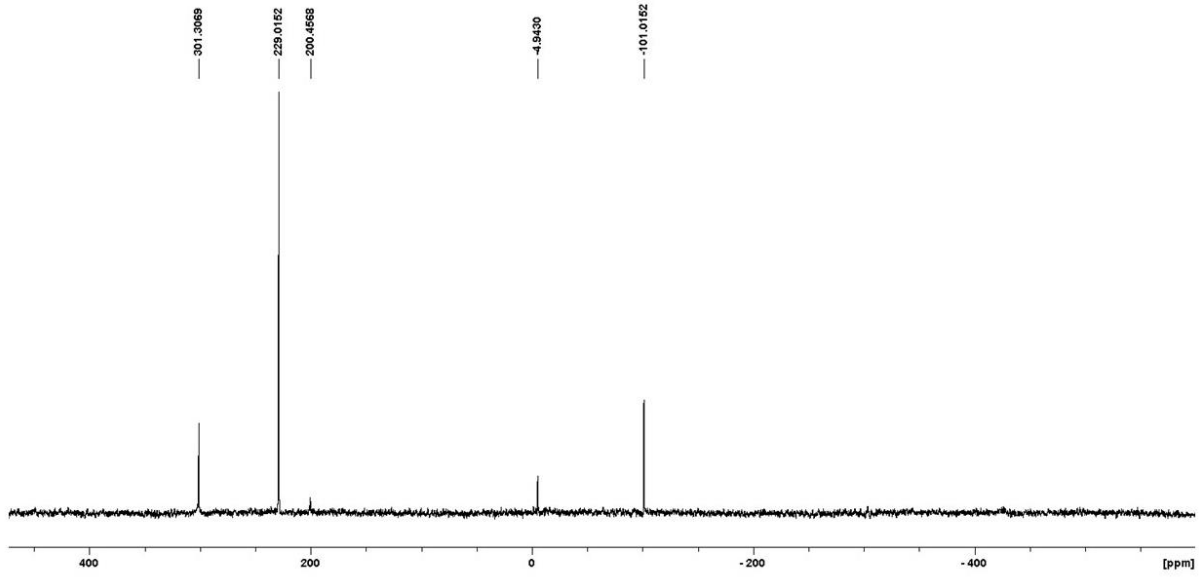


**Figure S 12** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (6 eq) ($C_6D_6$ capillary and $PPh_3$ as a reference δ =-4.9 ppm, 300K)

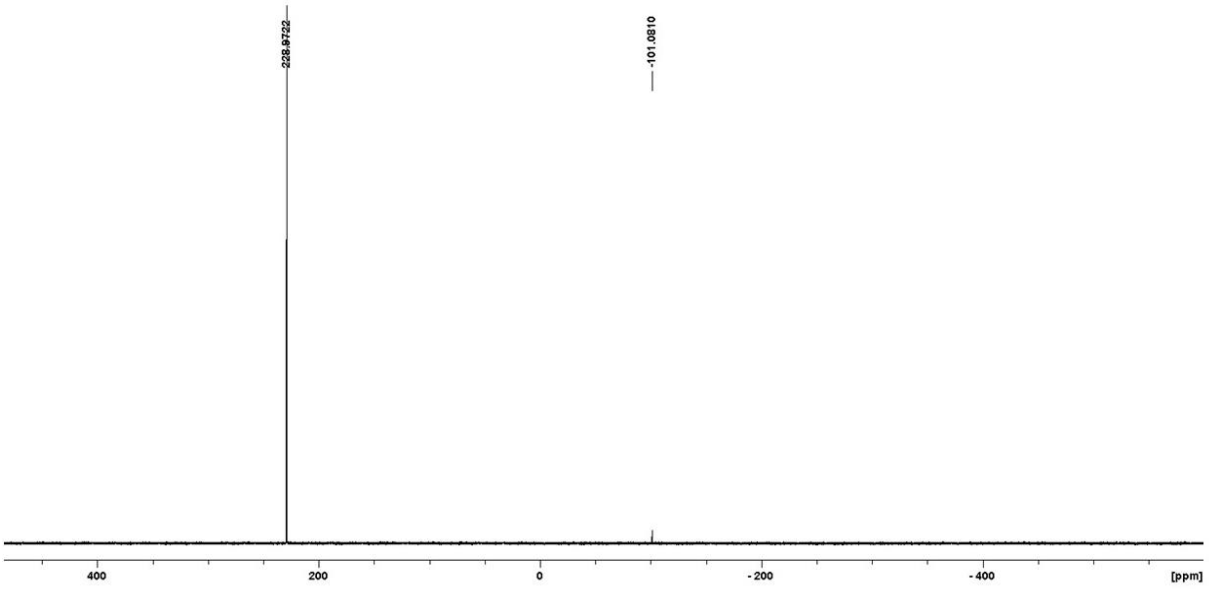


**Figure S 13** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (10 eq) ($C_6D_6$ capillary, 300K)

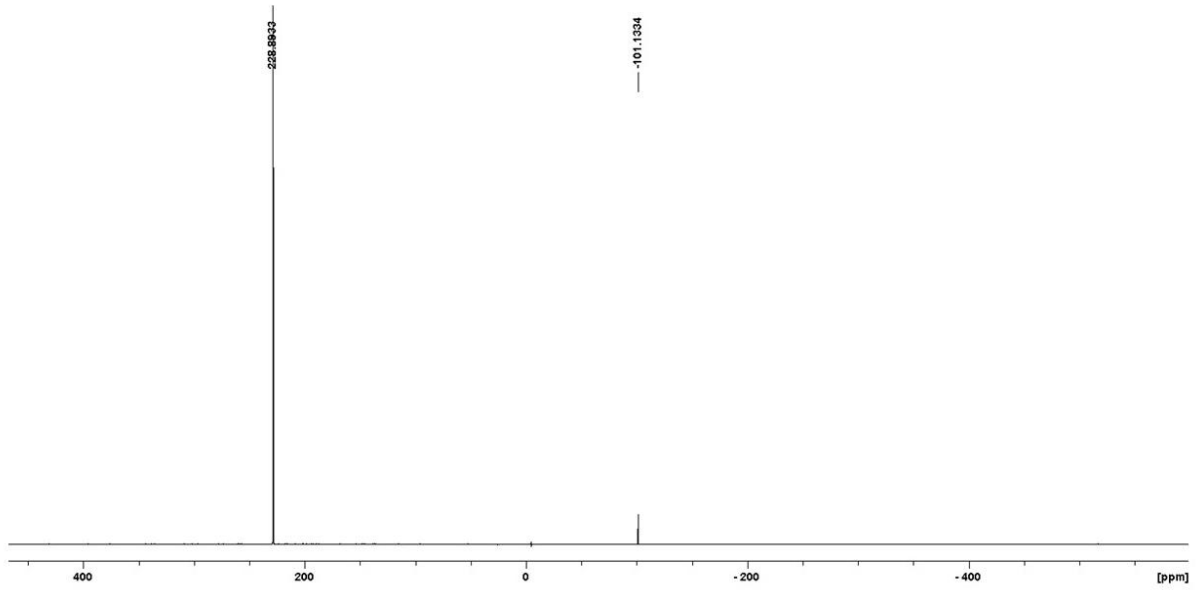


**Figure S 14** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (100 eq) ($C_6D_6$ capillary, 300K)

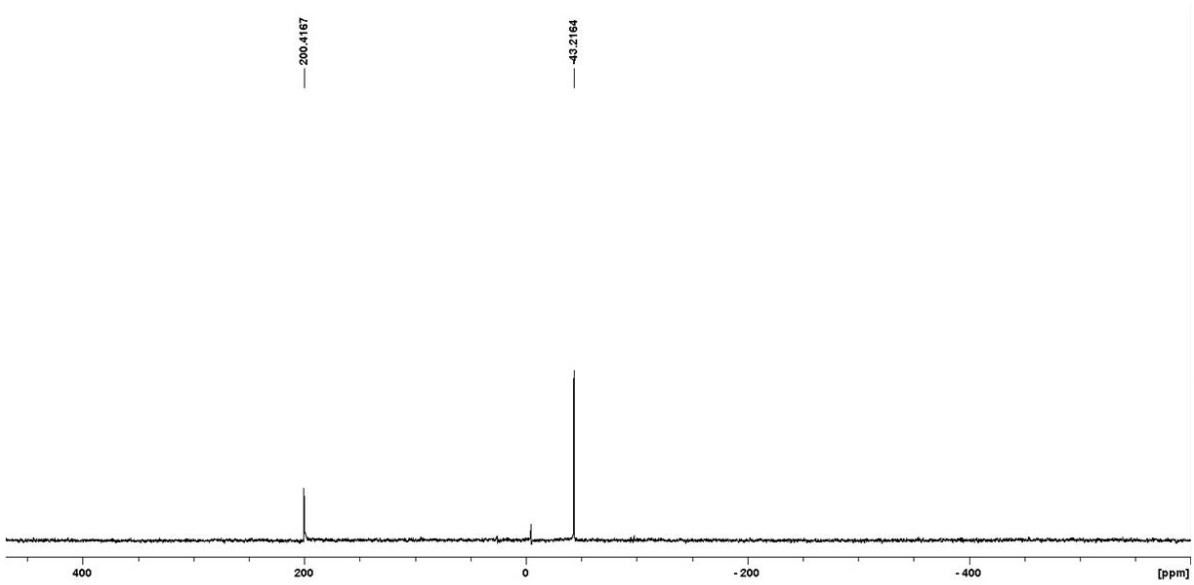


**Figure S 15** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $Br_2$ (1 eq) ($C_6D_6$ capillary, 300K)

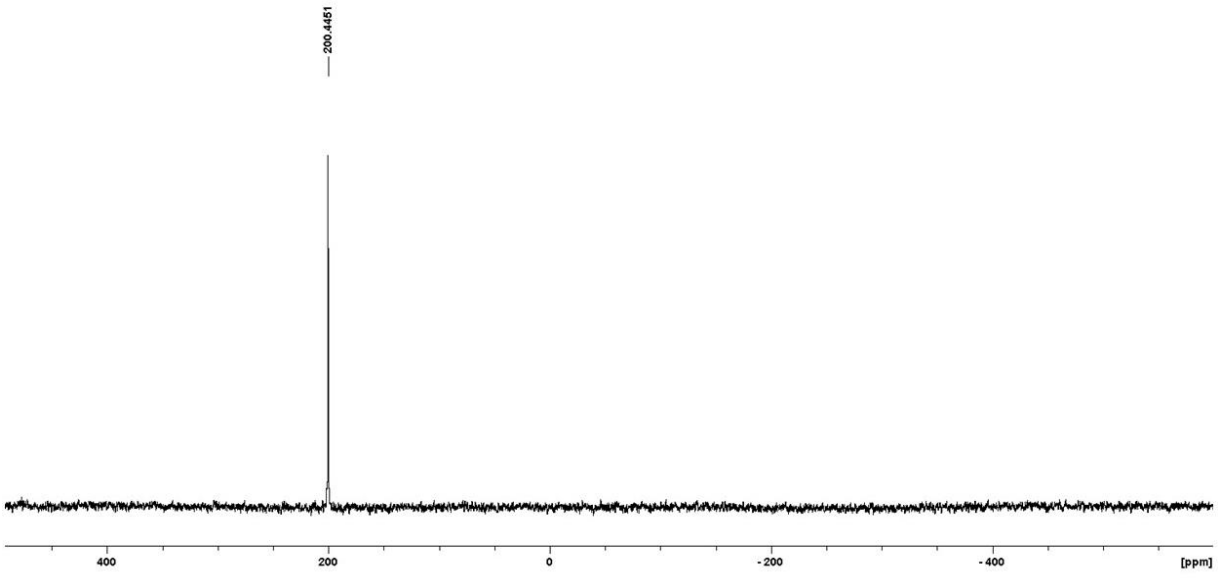


**Figure S 16** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $Br_2$ (2 eq) ($C_6D_6$ capillary, 300K)

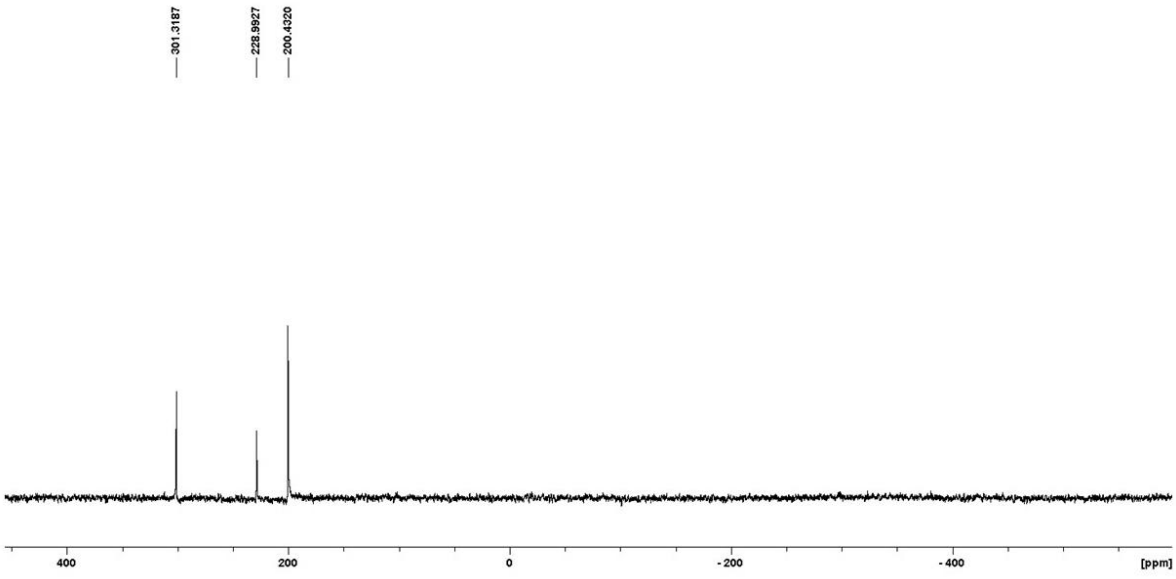


**Figure S 17** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $Br_2$ (3 eq) ($C_6D_6$ capillary, 300K)

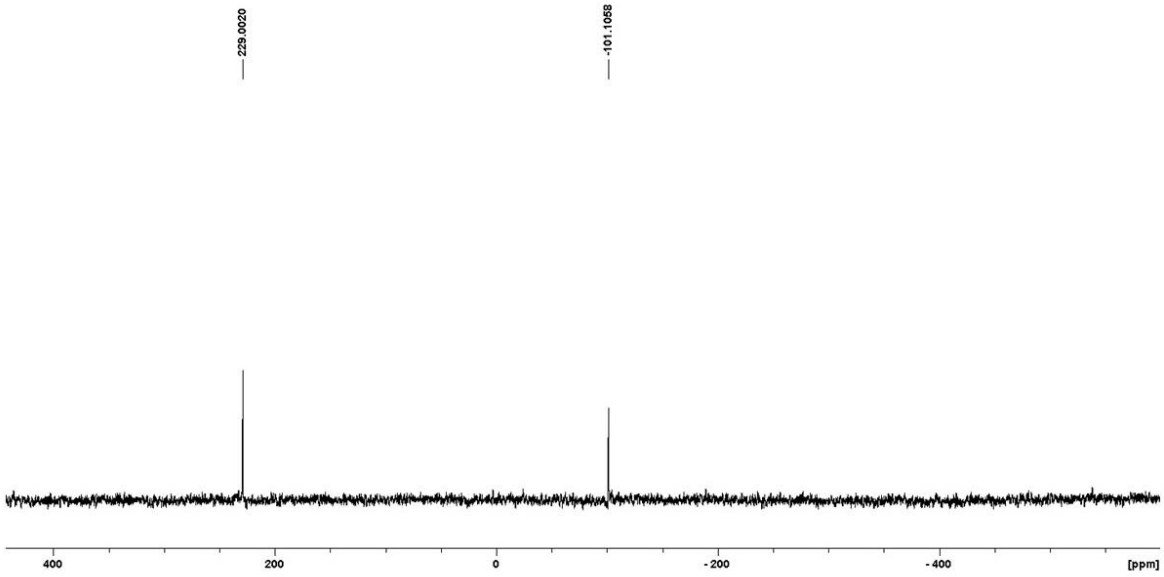


**Figure S 18** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $Br_2$ (6 eq) ($C_6D_6$ capillary, 300K)

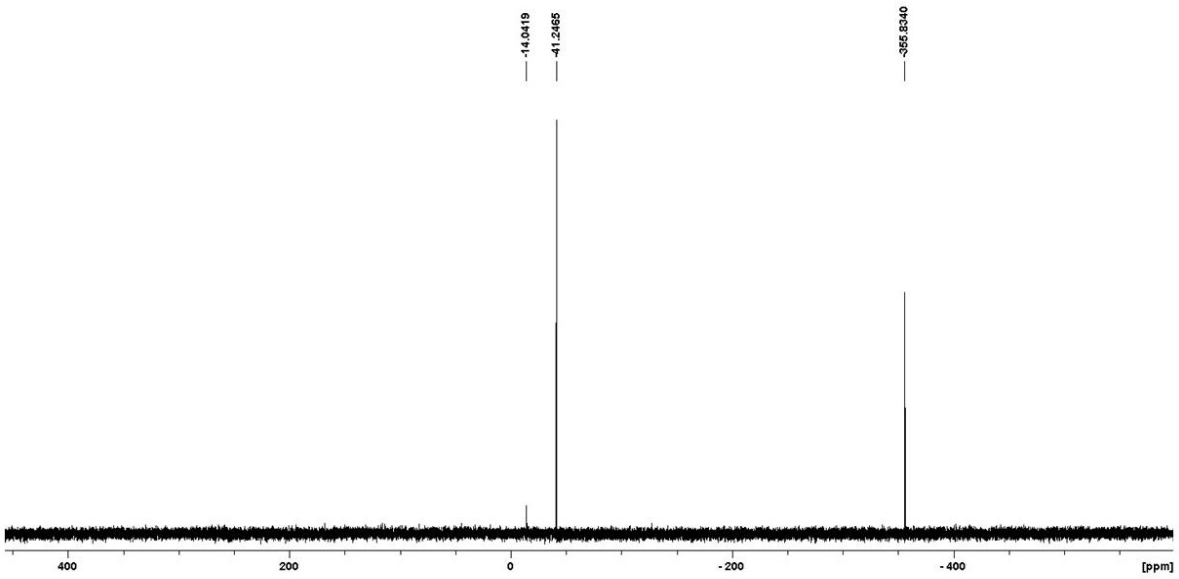


**Figure S 19** $^{31}P\{^{1}H\}$ NMR spectrum of **4a** after 2 hours at reflux in $CH_3CN$ ($C_6D_6$ capillary, 300K)

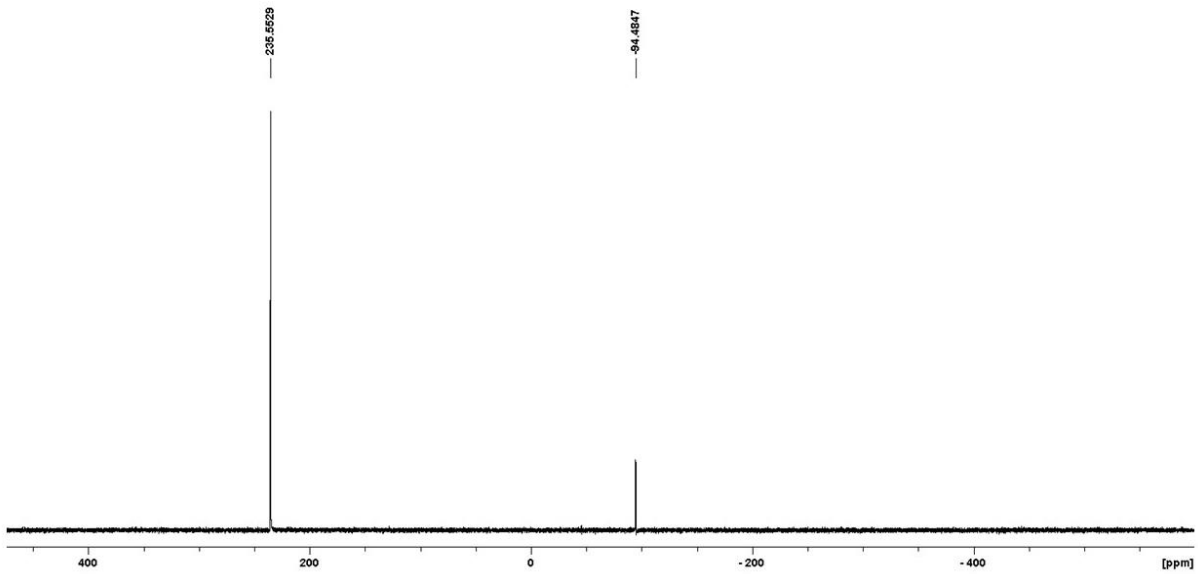


**Figure S 20** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (6 eq) after 2 hours at reflux in $CH_3CN$ ($C_6D_6$ capillary, 300K)

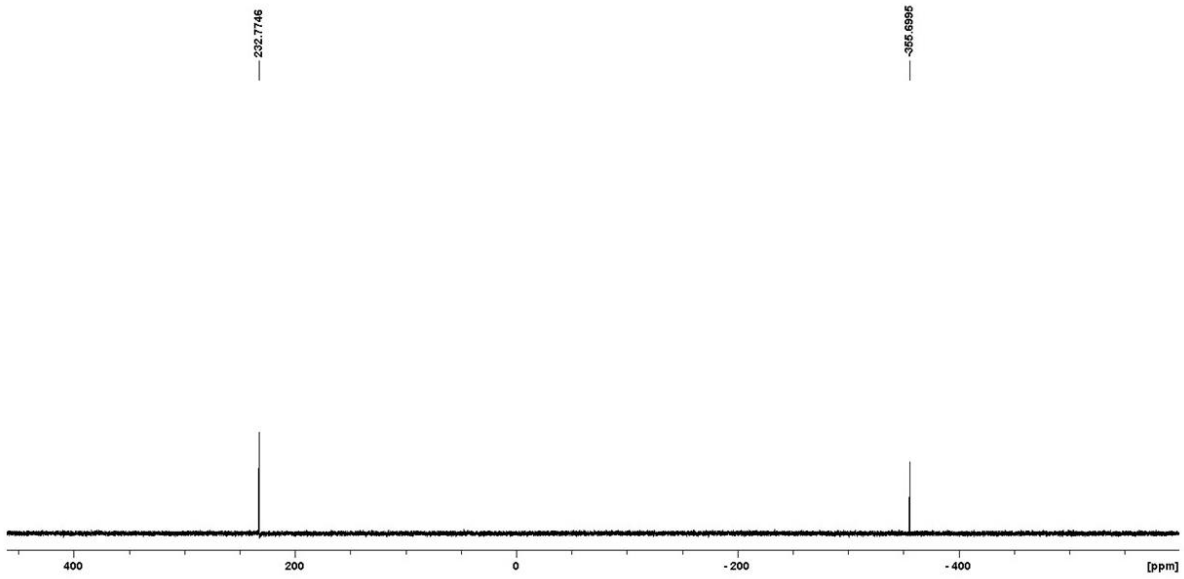


**Figure S 21** $^{31}P\{^{1}H\}$ NMR spectrum of the solution of the reaction between **1** (1 eq) and $PBr_5$ (1 eq) after 2 hours at reflux in $CH_3CN$ ($C_6D_6$ capillary, 300K)

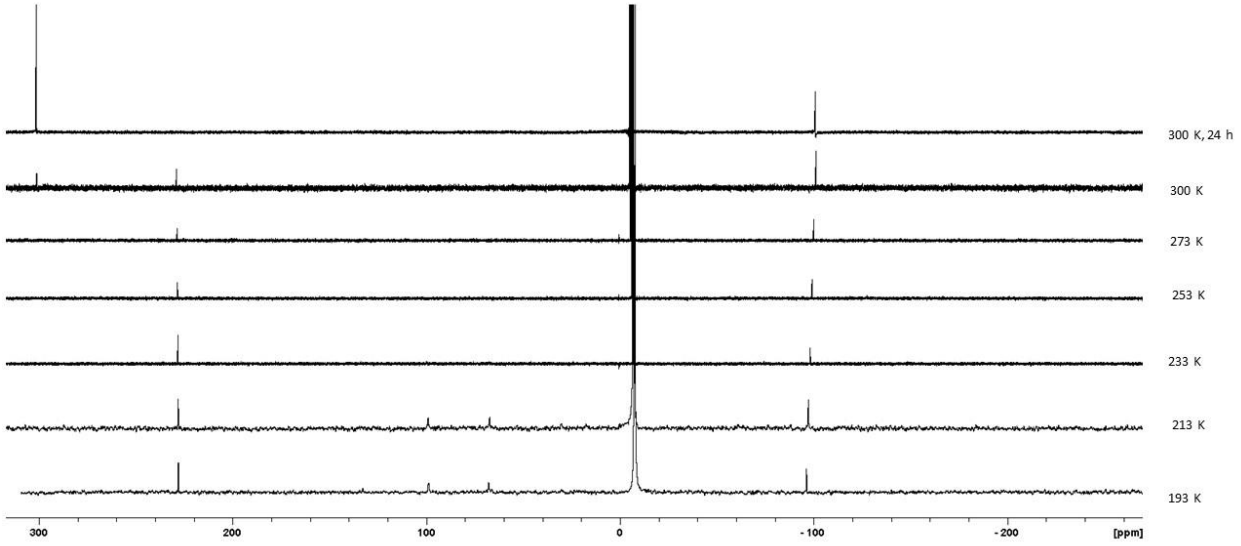


**Figure S 22** VT $^{31}P\{^{1}H\}$ NMR spectra of the solution of the reaction between **1** (1 eq) and $Br_2$ (6 eq) in $CD_2Cl_2$ ($CD_2Cl_2$ and $PPh_3$ as a reference δ =-4.9 ppm).

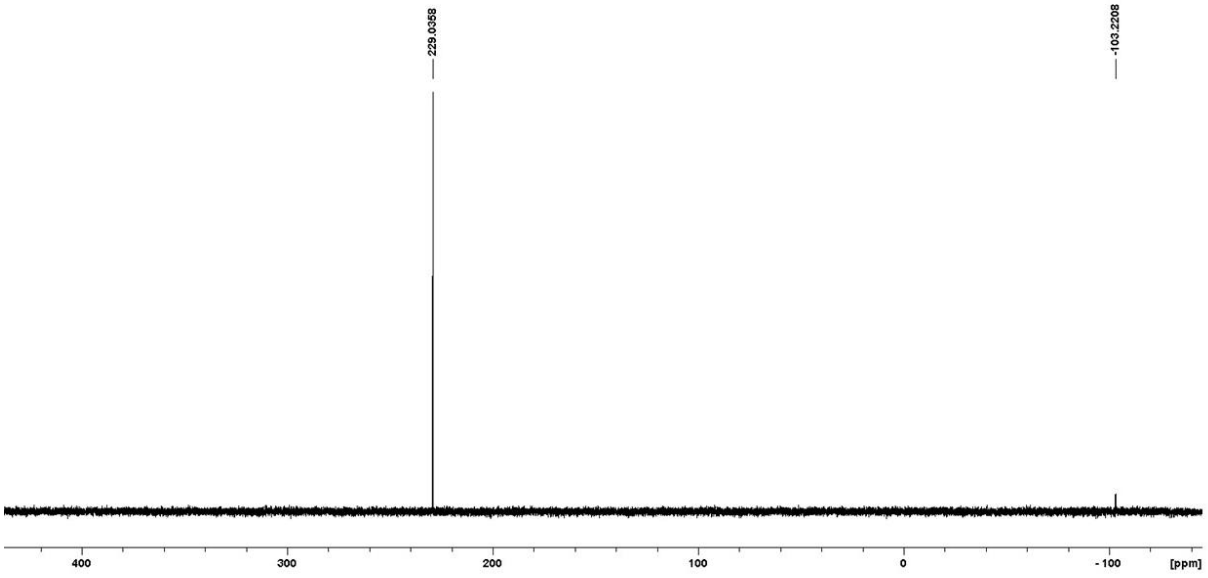


**Figure S 23** $^{31}P\{^{1}H\}$ NMR spectrum of $PBr_5$ ($C_6D_6$, 300K)

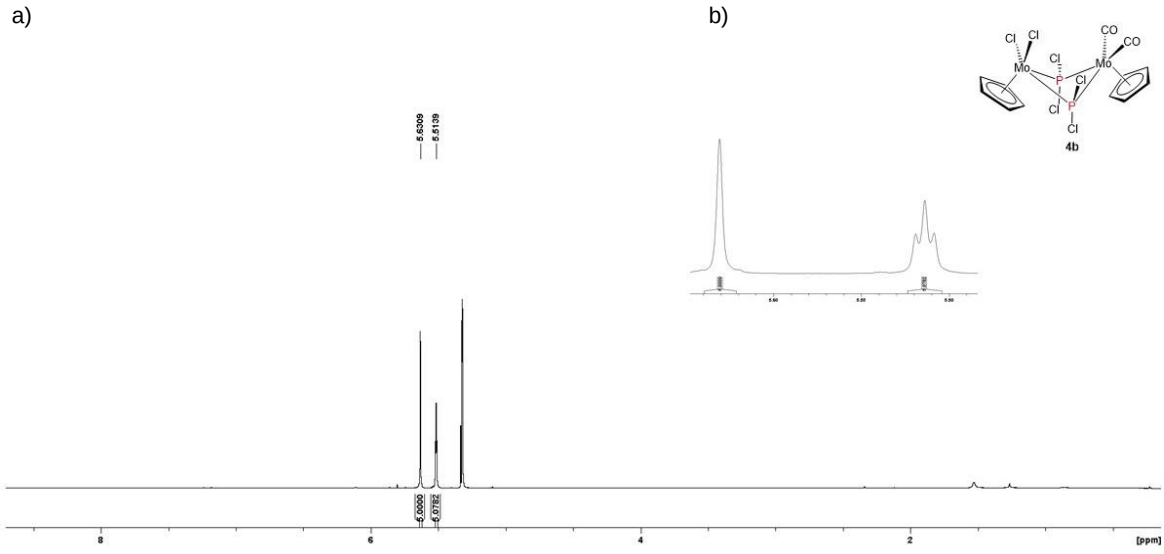


**Figure S 24** $^{1}H$ NMR spectrum of compound **4b** (a) ($CD_2Cl_2$, 300 K) and zoom on the signals (b)

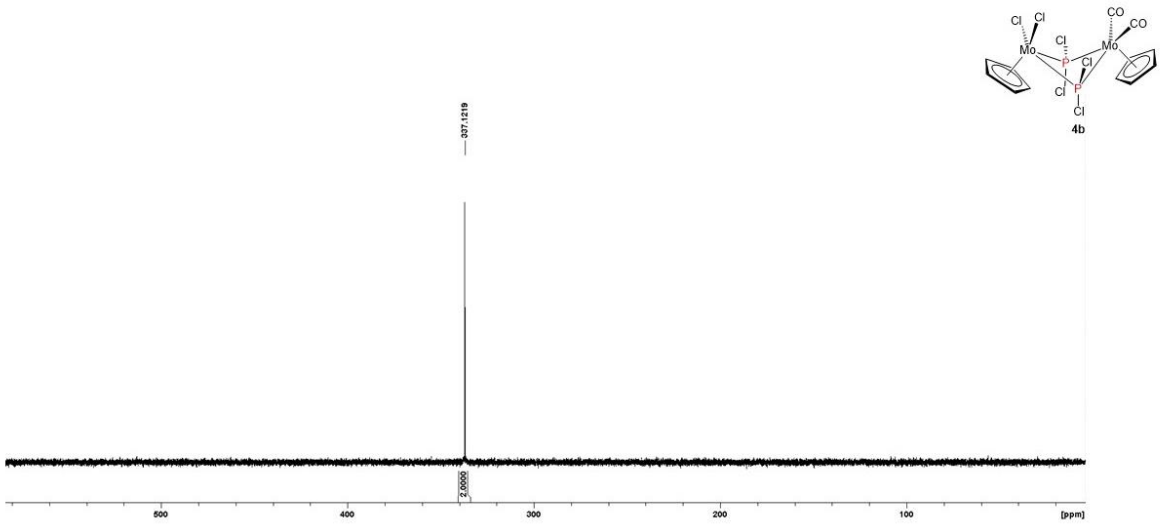


**Figure S 25** $^{31}P\{^{1}H\}$ NMR spectrum of compound **4b** ($CD_2Cl_2$, 300 K)

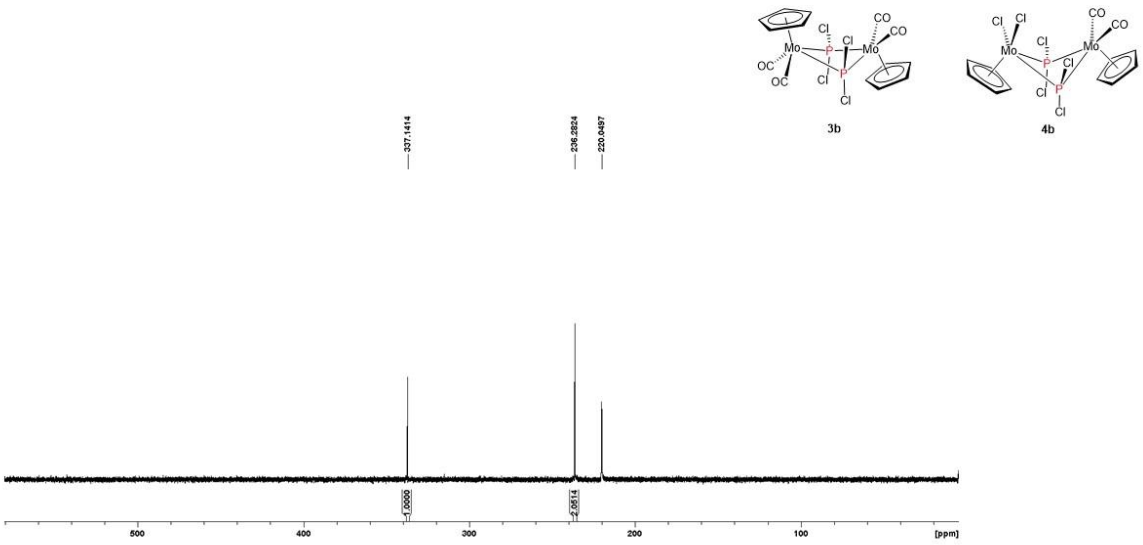


**Figure S 26** $^{31}P\{^{1}H\}$ NMR spectrum, positive region, of the solution of the reaction between 1 *(*1 eq*)* and $PCl_5$ (1 eq) ($CD_2Cl_2$, 300 K)

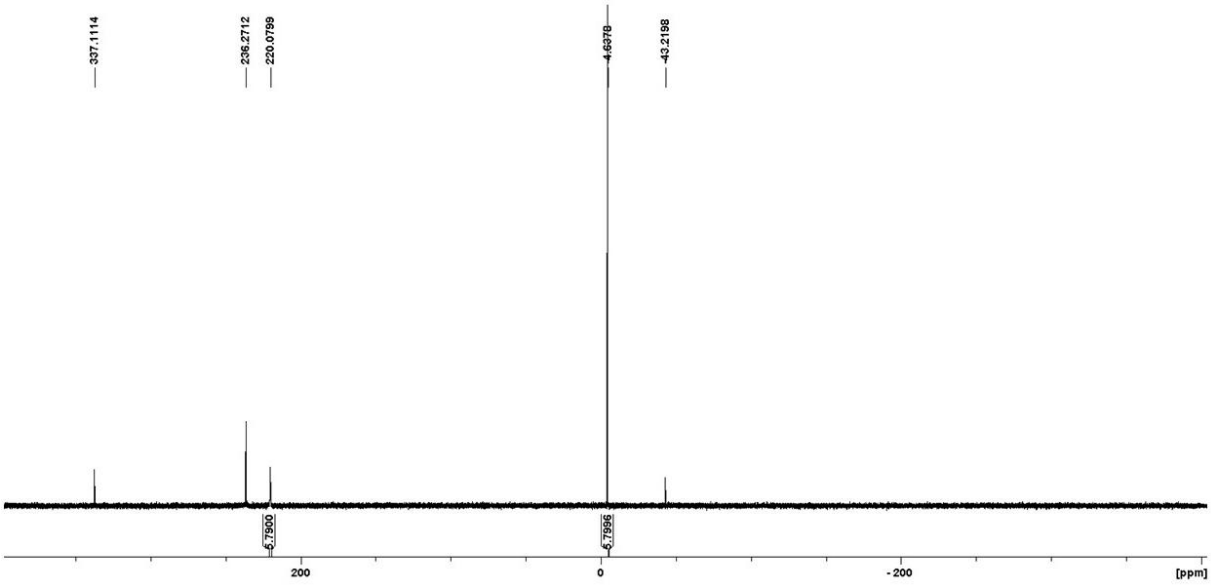


**Figure S 27** $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution of **1** with $PCl_5$ and $PPh_3$ as a reference ($CD_2Cl_2$, 300 K)

- mmol $PPh_3$ in the inner part of the Evans NMR tube: $5.7 \cdot 10^{-4}$
- mmol $PCl_5$ in the Evans NMR tube: $3.33 \cdot 10^{-3}$
- $\frac{PCl_5}{PPh_3} = \frac{3.33 \cdot 10^{-3}}{5.7 \cdot 10^{-4}} = 5.79$
- Integration $PPh_3 = 5.79$
- Integration $PCl_3 = 5.79$
- 5.79 out of 5.79 (**100%**) equals the amount of $PCl_3$ coming from $PCl_5$
- No $PCl_3$ comes from **1**

# 3Crystallographic Details

The crystals were selected and mounted on a Gemini Ultra diffractometer equipped with an AtlasS2 CCD detector (**4b**, **5**), on a GV50 diffractometer equipped with a TitanS2 detector (**2**, **3a**) and on a SuperNova diffractometer equipped with an Atlas detector (**4a**), respectively. All crystals were kept at a steady T = 123(1) K during data collection. Data collection and reduction were performed with **CrysAlispro** (Version 1.171.41.54a (**2**)[2], Version 1.171.38.46 (**4b**)[3], 1.171.39.37b (**3a**, **4a**), 1.171.39.46 (**5**))[4]. For the compounds (**3a**, **4a**, **4b**, **5**) a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK were applied. For compound **2** an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.
Using **Olex2**[5], all structures were solved by **ShelXT**[6] and a least square refinement on $F^2$ was carried out with **ShelXL**[7]. All non-hydrogens atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The images showing the compounds **2**-**5** were generated using **Olex2**.[5]

**Compound 2**: The asymmetric unit contains one molecule of the complex $[(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_4]$ and two only partly occupied $I_2$ molecules, which are additionally disordered over two positions (46:04; 12:12). One of these $I_2$ units (46% occupancy) forms with another I atom an $I_3$ unit. Further one of the four Mo atoms is disordered over two positions (67:33). The restraints SADI and SIMU were applied to describe these disorders. Additional, compound **2** was refined as a 2-component twin (BASF 0.51).
**Compound 3a**: The asymmetric unit contains one molecule of the complex $[CpMo(CO)_2(PBr_2)]_2$.
**Compound 4a**: The asymmetric unit contains one molecule of the complex $[CpMo(CO)_2(\mu_2\text{-}PBr_2)_2CpMoBr_2]$. The Cp ligand of the $[CpMo(CO)_2]$ fragment is disordered over two positions (66:34). To describe this disorder the SADI and SIMU restraints were applied. Further, compound **4a** was refined as a 2-component inversion twin (BASF: 0.18).
**Compound 4b**: The asymmetric unit contains one molecule of the complex $[CpMo(CO)_2(\mu_2\text{-}PCl_2)_2CpMoCl_2]$. The Cp ligand of the $[CpMo(CO)_2]$ fragment is disordered over two positions (57:43). To describe this disorder the SADI, ISOR and SIMU restraints were applied. Further, compound **4b** was refined as a 2-component inversion twin (BASF: 0.42).
**Compound 5**: The asymmetric unit contains one quarter of the complex $[CpMo(I)_2]_2[I_3]$.
CCDC-2039393 (**2**), CCDC-2039394 (**3a**), CCDC-2039395 (**4a**), CCDC-2039396 (**4b**) and CCDC-2039397 (**5)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Table S 1** Crystallographic details of the compounds **2**, **3a**, **3b** and **4b**

| **Compound** | **2** | **3a** | **4a** | **4b** |
|---|---|---|---|---|
| CCDC | 2039393 | 2039394 | 2039395 | 2039396 |
| Formula | $C_{20}H_{20}I_{8.48}Mo_4P_3$ | $C_{14}H_{10}Br_4Mo_2O_4P_2$ | $C_{12}H_{10}Br_6Mo_2O_2P_2$ | $C_{12}H_{10}Cl_6Mo_2O_2P_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 3.139 | 2.569 | 3.002 | 2.272 |
| $\mu$/mm$^{-1}$ | 65.336 | 20.225 | 25.457 | 20.141 |
| Formula Weight | 1813.14 | 815.68 | 919.48 | 652.72 |
| Color | black | dark black | dark black | light brown |
| Shape | block | block | block | plate |
| Size/mm$^3$ | 0.10×0.06×0.04 | 0.13×0.08×0.05 | 0.12×0.09×0.08 | 0.22×0.06×0.03 |
| $T$/K | 123(1) | 123.01(10) | 123(1) | 123 |
| Crystal System | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Flack Parameter | -0.022(9) | - | - | - |
| Hooft Parameter | -0.0219(2) | - | - | - |
| Space Group | $P2_1$ | $P2_1/n$ | $Pna2_1$ | $Pna2_1$ |
| $a$/Å | 10.6325(4) | 10.74440(10) | 14.9697(3) | 14.5924(8) |
| $b$/Å | 12.4167(3) | 13.7134(2) | 9.1775(2) | 8.9657(4) |
| $c$/Å | 15.1106(5) | 14.3200(2) | 14.8058(3) | 14.5870(5) |
| $\alpha$/° | 90 | 90 | 90 | 90 |
| $\beta$/° | 105.956(4) | 91.6200(10) | 90 | 90 |
| $\gamma$/° | 90 | 90 | 90 | 90 |
| V/Å$^3$ | 1918.05(11) | 2109.10(5) | 2034.09(7) | 1908.43(15) |
| $Z$ | 2 | 4 | 4 | 4 |
| $Z'$ | 1 | 1 | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | Cu K$_\alpha$ | Cu K$_\alpha$ | CuK$_\alpha$ | Cu K$_\alpha$ |
| $\Theta_{min}$/° | 3.042 | 4.465 | 5.655 | 5.792 |
| $\Theta_{max}$/° | 74.563 | 74.347 | 74.865 | 72.883 |
| Measured Refl's. | 13190 | 19909 | 13430 | 5703 |
| Ind't Refl's | 13190 | 4263 | 3808 | 2801 |
| Refl's with I > 2(I) | 12376 | 4205 | 3704 | 2606 |
| $R_{int}$ | 0.0832 | 0.0493 | 0.0615 | 0.0433 |
| Parameters | 398 | 235 | 264 | 264 |
| Restraints | 276 | 0 | 166 | 196 |
| Largest Peak | 1.991 | 0.812 | 1.042 | 1.083 |
| Deepest Hole | -0.955 | -1.261 | -0.799 | -1.022 |
| GooF | 1.084 | 1.096 | 1.088 | 1.040 |
| $wR_2$ (all data) | 0.1788 | 0.0753 | 0.0869 | 0.0991 |
| $wR_2$ | 0.1751 | 0.0748 | 0.0858 | 0.0970 |
| $R_1$ (all data) | 0.0659 | 0.0291 | 0.0387 | 0.0421 |
| $R_1$ | 0.0632 | 0.0285 | 0.0373 | 0.0388 |

**Table S 2** Crystallographic details of the compound **5**

| **Compound** | **5** |
|---|---|
| CCDC | 2039397 |
| Formula | $C_{10}H_{10}I_7Mo_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 3.824 |
| $\mu$/mm$^{-1}$ | 11.459 |
| Formula Weight | 1210.36 |
| Color | metallic dark brown |
| Shape | plate |
| Size/mm$^3$ | 0.08×0.08×0.02 |
| $T$/K | 123 |
| Crystal System | orthorhombic |
| Space Group | *Pbam* |
| $a$/Å | 8.6088(3) |
| $b$/Å | 14.8872(5) |
| $c$/Å | 8.2028(3) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/Å$^3$ | 1051.28(6) |
| $Z$ | 2 |
| $Z'$ | 0.25 |
| Wavelength/Å | 0.71073 |
| Radiation type | Mo $K_\alpha$ |
| $\Theta_{min}$/° | 3.618 |
| $\Theta_{max}$/° | 32.199 |
| Measured Refl's. | 5848 |
| Ind't Refl's | 1832 |
| Refl's with I > 2(I) | 1557 |
| $R_{int}$ | 0.0353 |
| Parameters | 50 |
| Restraints | 0 |
| Largest Peak | 1.163 |
| Deepest Hole | -0.944 |
| GooF | 1.027 |
| $wR_2$ (all data) | 0.0506 |
| $wR_2$ | 0.0479 |
| $R_1$ (all data) | 0.0354 |
| $R_1$ | 0.0254 |

a) b)

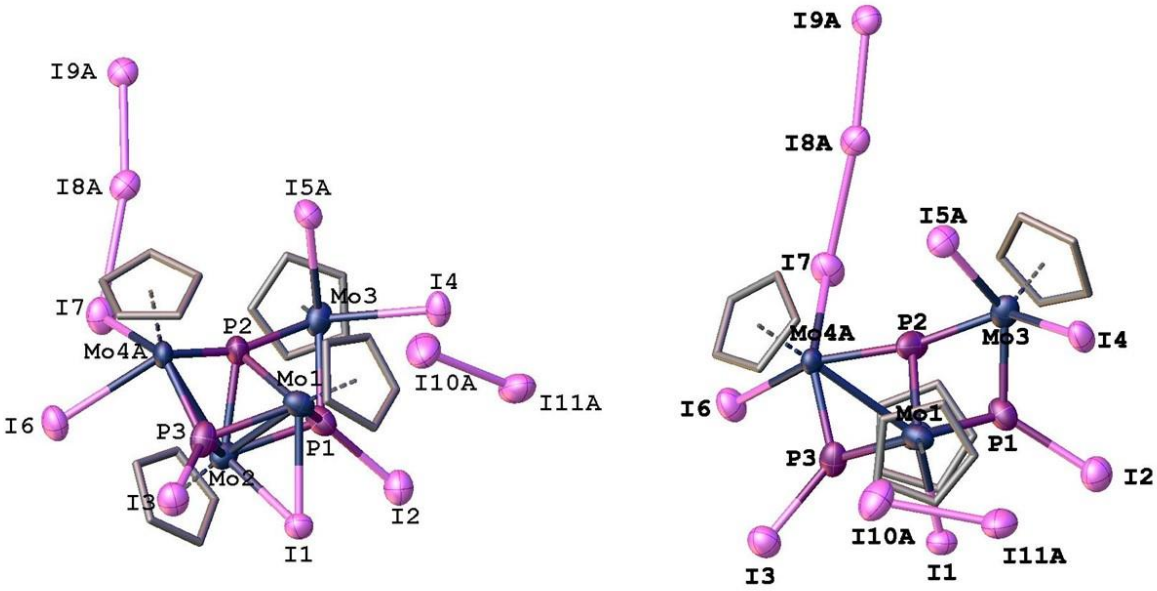


**Figure S 28** Side (a) and front (b) view of the part 1 of the molecular structure of **2** with thermal ellipsoid at 50% probability level. The hydrogen atoms and the part 2 are omitted for clarity

**Table S 3** Selected bond lengths and angles of **2**

| Atom | Atom | Length/Å |
|---|---|---|
| Mo1 | Mo2 | 2.740(3) |
| Mo1 | P1 | 2.423(7) |
| Mo1 | P2 | 2.523(8) |
| Mo1 | P3 | 2.387(8) |
| Mo2 | P1 | 2.421(8) |
| Mo2 | P2 | 2.408(9) |
| Mo2 | P3 | 2.398(7) |
| Mo3 | P1 | 2.390(9) |
| Mo3 | P2 | 2.330(8) |
| Mo4A | P2 | 2.283(11) |
| Mo4A | P3 | 2.261(12) |
| P1 | P2 | 2.568(12) |
| I8A | I9A | 2.764(6) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| P1 | Mo1 | P2 | 62.5(3) |
| P3 | Mo1 | P2 | 78.8(3) |
| P2 | Mo2 | P1 | 64.2(3) |
| P2 | Mo3 | P1 | 65.9(3) |
| P3 | Mo4A | P2 | 86.7(4) |
| P2 | Mo4A | Mo2 | 50.0(3) |
| Mo4A | P2 | Mo1 | 87.0(3) |
| Mo4A | P3 | Mo1 | 90.9(4) |
| Mo4A | P2 | Mo3 | 161.9(5) |

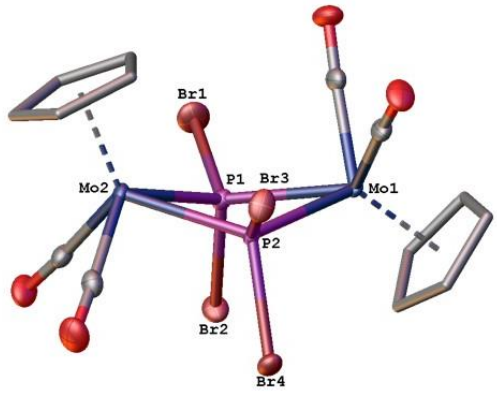


**Figure S 29:** Molecular structure of **3a** with thermal ellipsoid at 50% probability level. The hydrogen atoms are omitted for clarity

**Table S 4** Selected bond lengths and angles of **3a**

| Atom | Atom | Length/Å |
|---|---|---|
| Mo1 | P2 | 2.4641(8) |
| Mo1 | P1 | 2.4769(8) |
| Mo2 | P2 | 2.4714(8) |
| Mo2 | P1 | 2.4564(8) |
| Br2 | P1 | 2.2850(9) |
| Br3 | P2 | 2.2773(9) |
| Br4 | P2 | 2.2738(8) |
| Br1 | P1 | 2.2829(9) |
| P2 | P1 | 2.5856(11) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| P2 | Mo1 | P1 | 63.11(3) |
| P1 | Mo2 | P2 | 63.30(3) |
| Mo1 | P2 | Mo2 | 112.26(3) |
| Mo1 | P2 | P1 | 58.69(3) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| Mo2 | P2 | P1 | 58.07(3) |
| Mo1 | P1 | P2 | 58.20(3) |
| Mo2 | P1 | Mo1 | 112.34(3) |
| Mo2 | P1 | P2 | 58.63(3) |

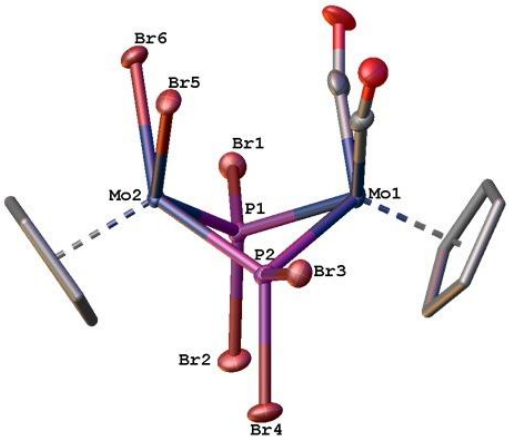


**Figure S 30:** Molecular structure of **4a** with thermal ellipsoid at 50% probability level. The hydrogen atoms and the second part of the disordered Cp ligand are omitted for clarity

a) b)

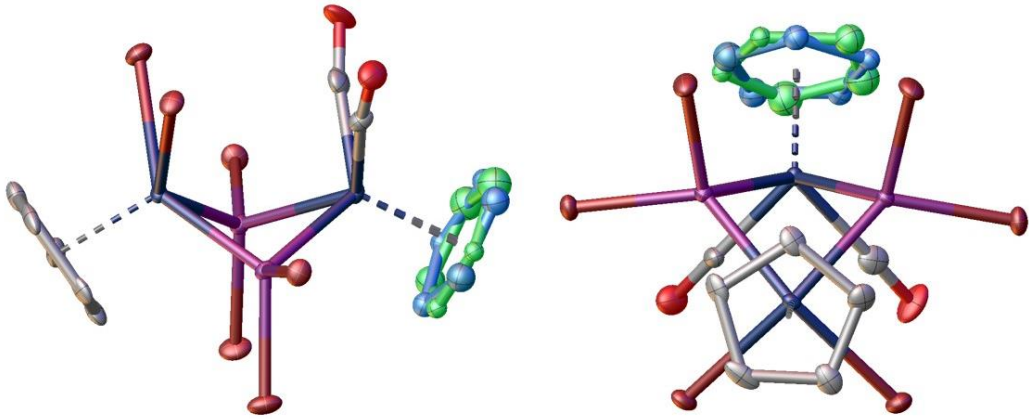

**Figure S 31** Side (a) and front (b) view of the molecular structure of **4a** with thermal ellipsoid at 50% probability level. The disordered Cp ligand is highlighted blue (part 1) and green (part 2). The hydrogen atoms are omitted for clarity

**Table S 5** Selected bond lengths and angles of **4a**

| Atom | Atom | Length/Å |
|---|---|---|
| Mo2 | P2 | 2.356(3) |
| Mo2 | P1 | 2.365(3) |
| Mo1 | P1 | 2.432(5) |
| Mo1 | P2 | 2.426(3) |
| Br1 | P1 | 2.238(3) |
| Br4 | P2 | 2.243(3) |
| Br2 | P1 | 2.239(3) |
| Br3 | P2 | 2.225(3) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| P2 | Mo1 | P1 | 77.09(9) |
| Mo1 | P2 | Mo2 | 86.86(9) |
| Mo1 | P1 | Mo2 | 86.50(9) |

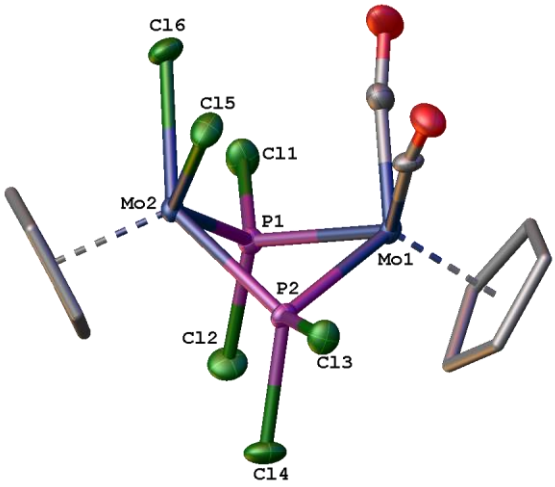


**Figure S 32** Molecular structure of **4b** with thermal ellipsoid at 50% probability level. The hydrogen atoms and the second part of the disordered Cp ligand are omitted for clarity

a)

b)

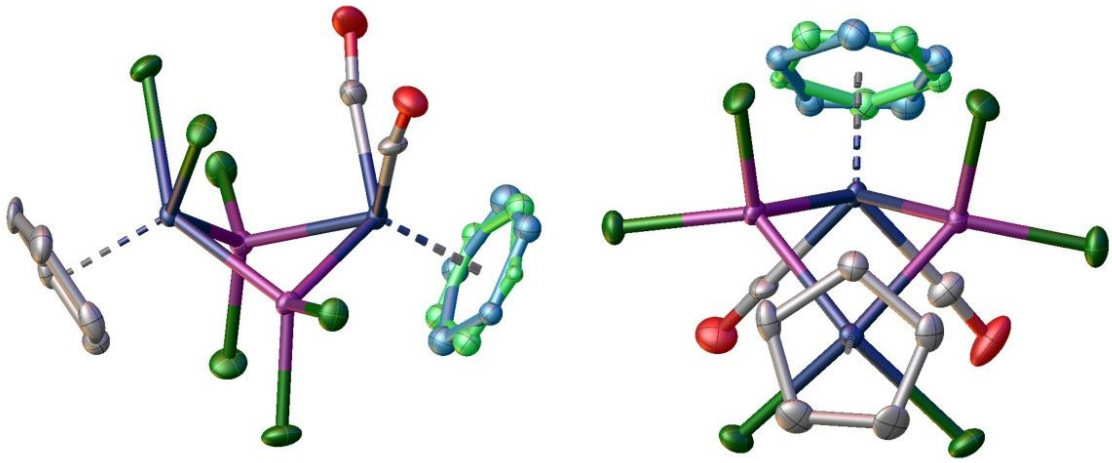

**Figure S 33** Side (a) and front (b) view of the molecular structure of **4b** with thermal ellipsoid at 50% probability level. The disordered Cp ligand is highlighted blue (part 1) and green (part 2)

**Table S 6** Selected bond lengths and angles of **4b**

| Atom | Atom | Length/Å |
|---|---|---|
| Mo1 | P2 | 2.407(3) |
| Mo1 | P1 | 2.426(3) |
| Mo2 | P1 | 2.351(3) |
| Mo2 | P2 | 2.344(3) |
| P2 | Cl4 | 2.056(4) |
| P2 | Cl3 | 2.071(3) |
| Cl1 | P1 | 2.060(4) |
| P1 | Cl2 | 2.069(4) |

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| P2 | Mo1 | P1 | 74.23(9) |
| Mo1 | P2 | Mo2 | 87.08(9) |
| Mo1 | P1 | Mo2 | 86.49(8) |

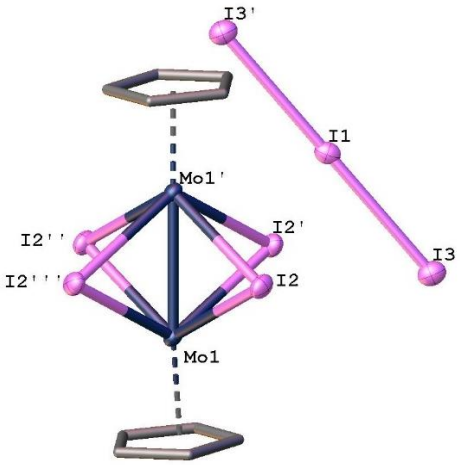


**Figure S 34** Molecular structure of **5** with thermal ellipsoid at 50% probability level. The hydrogen atoms are omitted for clarity

**Table S 7** Selected bond lengths and angles of **5**

| Atom | Atom | Length/Å |
|---|---|---|
| Mo1 | Mo1’ | 2.7032(8) |
| Mo1 | I2 | 2.7769(4) |
| I1 | I3 | 2.9319(4) |

| Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|
| I3’ | I1 | I3 | 180.000(14) |
| I2 | Mo1 | I2’’’ | 75.992(11) |
| Mo1 | I2 | Mo1’ | 58.225(15) |

# 4 Computational Details

All calculations for [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) have been performed with the TURBOMOLE program package.[8,9] The geometry has been optimized in different spin states using the BP86,[10,11] B3LYP,[12,13] PBE0,[Fehler! Textmarke nicht definiert.14,15] B97-D,[16] TPSS[17] and TPSSh[18] functionals together with the def2-TZVP[19,20] basis set (cf. Table 1). To speed up the geometry optimization the Resolution of Identity (RI)[20,21] and the Multipole Accelerated Resolution-of-the-Identity (MARI-J)[22] approximations has been used. The final energy of the molecules was determined by single point calculations without using the RI formalism.

The DFT calculations for compounds **3, 4a** and **3, 4b** have been performed with Gaussian 09[23] using the B3LYP functional together with the def2-TZVP basis set.

## [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (2)

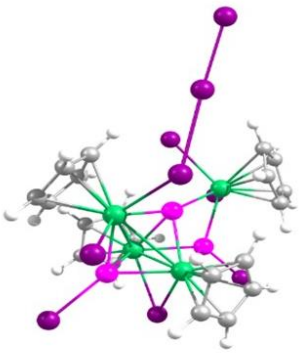

**Table S 8** Relative energies (kJ·mol$^{-1}$) of [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) in different spin states calculated using different functionals together with the def2-TZVP basis set.

| | BP86 | TPSS | TPSSH | B3LYP | PBE0 | B97-D |
|---|---|---|---|---|---|---|
| **unrest. singl.** | 0.00 | 0.00 | 6.43 | 18.49 | 14.25 | 9.32 |
| **triplet** | 5.01 | 2.88 | 0.00 | 0.00 | 0.00 | 0.00 |
| **quintet** | 57.52 | 62.84 | 52.21 | 25.12 | 38.92 | 35.97 |
| **septet** | 95.85 | 104.05 | 78.45 | 23.34 | 46.88 | 52.05 |

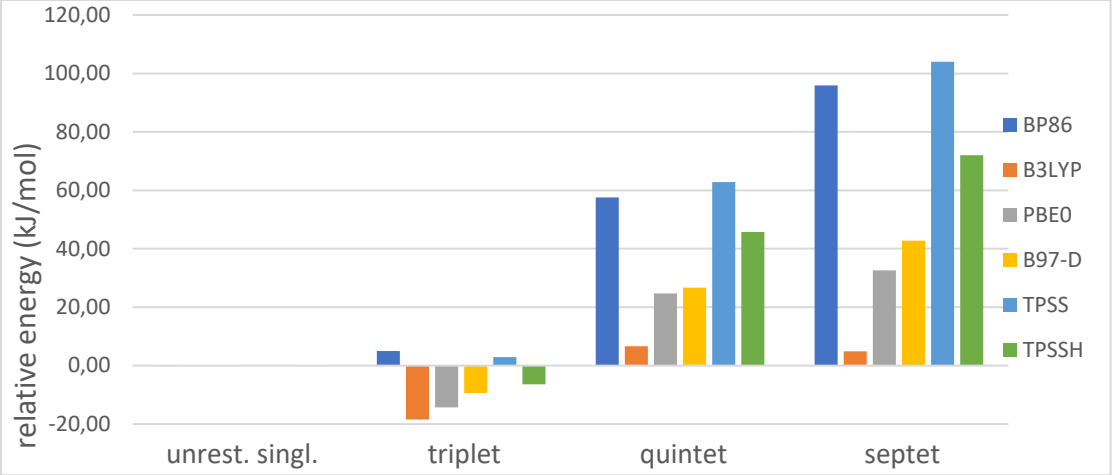


**Figure S 35** Relative energies (kJ·mol$^{-1}$) of [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) in different spin states calculated using different functionals together with the def2-TZVP basis set.

**Table S 9** Cartesian coordinates of the optimized geometry of [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) in unrestricted singlet spin state at the B3LYP/def2-TZVP level. Total energy = −4750.54510486619 a.u.; <S*S> = 0.00

| | | | |
|---|---|---|---|
| Mo | -1.6691341 | -0.0046287 | 1.4372379 |
| Mo | -1.6619085 | 0.0595124 | -1.3142437 |
| Mo | 0.2121058 | 2.2451420 | 0.2542290 |
| Mo | 1.1669585 | -2.3063722 | -0.5798797 |
| P | -2.1051505 | 1.9493541 | 0.0979836 |
| P | 0.4118841 | -0.1021393 | 0.0954354 |
| P | -1.1971324 | -1.9980314 | 0.0238877 |
| I | -3.9055971 | 3.6083441 | -0.1132614 |
| I | -2.6981361 | -4.0526775 | 0.1762704 |
| I | -4.1306992 | -0.4753063 | 0.0606598 |
| I | -0.6182858 | 4.1079420 | 2.3464937 |
| I | 0.4470732 | -4.0005985 | -2.6819917 |
| I | 2.8658621 | -1.0582070 | -2.4726445 |
| I | 2.2859510 | 1.7275826 | 2.3484580 |
| I | 5.3582042 | 1.0310682 | 1.3591746 |
| I | 7.9887645 | 0.4824726 | 0.6501523 |
| C | -1.0202591 | 0.7032384 | 3.5751085 |
| C | -2.8905740 | -0.6041158 | 3.4014968 |
| C | -0.5997134 | -0.6491983 | 3.4307083 |
| C | -2.4385889 | 0.7304372 | 3.5551636 |
| H | -3.0540304 | 1.6103357 | 3.6444170 |
| C | -1.7617068 | -1.4576754 | 3.3276017 |
| C | -0.8205189 | -0.5306700 | -3.4420985 |
| C | -2.5232598 | 1.0193302 | -3.3190442 |
| H | -3.0686002 | 1.9491904 | -3.3125453 |
| C | -2.0467792 | -1.2317219 | -3.2722193 |
| C | -1.1201223 | 0.8561339 | -3.4720230 |
| C | -3.0884332 | -0.2760634 | -3.2153642 |
| H | -0.3806243 | 1.5560560 | 3.7125009 |
| H | -3.9178717 | -0.9228519 | 3.3362391 |
| H | 0.4208728 | -0.9875614 | 3.4590943 |
| H | -1.8011741 | -2.5287658 | 3.2130706 |
| H | 0.1515196 | -0.9760818 | -3.5699353 |
| H | -2.1520626 | -2.3024511 | -3.2151027 |
| H | -0.4129139 | 1.6434623 | -3.6568676 |
| H | -4.1354321 | -0.4947073 | -3.0898576 |
| C | 2.2238564 | 2.8612585 | -0.8936486 |
| H | 3.1461032 | 2.3412703 | -0.6937760 |
| C | 0.1862242 | 3.4190256 | -1.7880898 |
| C | 1.7411913 | 4.0182127 | -0.2233035 |
| C | 1.2629148 | 2.4797688 | -1.8474831 |
| C | 0.5001646 | 4.3788997 | -0.8043507 |
| C | 3.2323485 | -2.7201692 | 0.5085861 |
| C | 1.2641233 | -3.1960682 | 1.5787044 |
| C | 1.4806848 | -4.2174329 | 0.6139155 |
| H | 0.8470282 | -5.0688126 | 0.4358425 |
| C | 2.7121648 | -3.9165582 | -0.0519307 |
| H | 3.1604218 | -4.4882696 | -0.8459446 |
| C | 2.3416090 | -2.2769998 | 1.5088623 |
| H | -0.6943499 | 3.4335097 | -2.4055122 |
| H | 2.2278830 | 4.5288729 | 0.5897620 |
| H | 1.3699045 | 1.6327061 | -2.5020481 |
| H | -0.1189607 | 5.2085430 | -0.5099475 |
| H | 4.1315383 | -2.2120460 | 0.2058145 |
| H | 0.4311503 | -3.1483626 | 2.2565764 |
| H | 2.4635126 | -1.3771254 | 2.0896666 |

**Table S 10** Cartesian coordinates of the optimized geometry of $[(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_3(I_3)]$ (**2**) in triplet spin state at the B3LYP/def2-TZVP level. Total energy = −4750.55214680069 a.u.; <S*S> = 2.03

| | | | |
|---|---|---|---|
| Mo | -1.6886549 | 0.0411364 | 1.3936624 |
| Mo | -1.7755657 | 0.1792134 | -1.3479962 |
| Mo | 0.1971779 | 2.2438580 | 0.2018025 |
| Mo | 1.2645246 | -2.4041062 | -0.4908133 |
| P | -2.1428385 | 2.0273773 | 0.1095969 |
| P | 0.3253684 | -0.1065435 | -0.0574132 |
| P | -1.2363818 | -1.8933115 | -0.0811059 |
| I | -3.9016794 | 3.7446468 | 0.0277417 |
| I | -2.7150710 | -3.9830408 | 0.0812172 |
| I | -4.1913629 | -0.3969357 | 0.0699133 |
| I | -0.5207503 | 4.0823928 | 2.3618483 |
| I | 0.5048464 | -4.0422919 | -2.5879390 |
| I | 2.9529446 | -1.0224477 | -2.2461295 |
| I | 2.3162625 | 1.6265431 | 2.2213130 |
| I | 5.4141298 | 1.0500876 | 1.2479637 |
| I | 8.0755847 | 0.5908097 | 0.5878095 |
| C | -0.9665149 | 0.6768958 | 3.5360491 |
| C | -2.8970586 | -0.5412643 | 3.3739284 |
| C | -0.6108842 | -0.6874419 | 3.3500249 |
| C | -2.3828285 | 0.7670777 | 3.5465955 |
| H | -2.9559492 | 1.6714282 | 3.6674125 |
| C | -1.8097236 | -1.4421541 | 3.2509141 |
| C | -0.8161643 | -0.3052014 | -3.4608402 |
| C | -2.7227300 | 0.9938115 | -3.3736243 |
| H | -3.3902840 | 1.8400616 | -3.3752373 |
| C | -1.9311437 | -1.1689058 | -3.3257286 |
| C | -1.3110633 | 1.0304389 | -3.4994289 |
| C | -3.0988461 | -0.3697518 | -3.2634083 |
| H | -0.2872294 | 1.4973190 | 3.6794629 |
| H | -3.9391171 | -0.8108181 | 3.3237679 |
| H | 0.3930557 | -1.0716904 | 3.3428866 |
| H | -1.8984794 | -2.5066753 | 3.1076852 |
| H | 0.2120179 | -0.6153816 | -3.5558962 |
| H | -1.8887626 | -2.2440630 | -3.2742814 |
| H | -0.7252617 | 1.9145651 | -3.6711322 |
| H | -4.1041760 | -0.7395601 | -3.1497398 |
| C | 2.1694462 | 2.8140561 | -1.0153566 |
| H | 3.0675763 | 2.2334173 | -0.8862256 |
| C | 0.1249394 | 3.5302925 | -1.7778914 |
| C | 1.7918075 | 3.9667391 | -0.2750284 |
| C | 1.1390475 | 2.5347050 | -1.9338343 |
| C | 0.5478405 | 4.4242666 | -0.7741020 |
| C | 3.2930589 | -2.8379352 | 0.7199926 |
| C | 1.2736444 | -3.3816087 | 1.6629137 |
| C | 1.6088488 | -4.3975811 | 0.7331693 |
| H | 1.0130244 | -5.2647603 | 0.5022444 |
| C | 2.8600368 | -4.0595220 | 0.1486670 |
| H | 3.3750026 | -4.6222046 | -0.6124157 |
| C | 2.3138484 | -2.4124452 | 1.6506494 |
| H | -0.7861554 | 3.6222068 | -2.3425334 |
| H | 2.3481338 | 4.4113780 | 0.5321154 |
| H | 1.1594982 | 1.7211369 | -2.6353425 |
| H | -0.0042536 | 5.2740270 | -0.4122108 |
| H | 4.1972984 | -2.3049600 | 0.4777525 |
| H | 0.3901645 | -3.3666413 | 2.2779878 |
| H | 2.3698009 | -1.5106449 | 2.2385674 |

**Table S 11** Cartesian coordinates of the optimized geometry of $[(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_3(I_3)]$ (**2**) in quintet spin state at the B3LYP/def2-TZVP level. Total energy = −4750.54258024538 a.u.; <S*S> = 6.11

| | | | |
|---|---|---|---|
| Mo | -1.7768317 | 0.0139544 | 1.3731729 |
| Mo | -2.0424195 | -0.0675485 | -1.4164554 |
| Mo | 0.4536313 | 2.3876441 | 0.4448489 |
| Mo | 1.2090265 | -2.3256873 | -0.5409121 |
| P | -1.8864540 | 1.9553128 | -0.0625704 |
| P | 0.1687054 | -0.0011826 | -0.1588993 |
| P | -1.2663767 | -1.9603164 | -0.0253214 |
| I | -3.5473603 | 3.7629189 | -0.3979641 |
| I | -2.6933043 | -4.0505217 | 0.2182219 |
| I | -4.3445945 | -0.3435015 | 0.1402023 |
| I | -0.4947573 | 4.1429037 | 2.4466108 |
| I | 0.4539160 | -4.0486302 | -2.5822501 |
| I | 2.8472148 | -0.9757360 | -2.3725487 |
| I | 2.3885633 | 1.5629274 | 2.4207766 |
| I | 5.5192890 | 1.1242781 | 1.3699970 |
| I | 8.1541019 | 0.7419511 | 0.6036662 |
| C | -1.0313600 | 0.6809921 | 3.4930353 |
| C | -2.9690905 | -0.5323879 | 3.3802536 |
| C | -0.6851440 | -0.6899495 | 3.3232811 |
| C | -2.4482314 | 0.7795991 | 3.5120843 |
| H | -3.0168545 | 1.6876386 | 3.6254938 |
| C | -1.8898319 | -1.4396361 | 3.2640228 |
| C | -1.0018629 | -0.4081573 | -3.5332754 |
| C | -2.9727921 | 0.7744851 | -3.4300445 |
| H | -3.6820685 | 1.5857308 | -3.3908714 |
| C | -2.0674886 | -1.3395909 | -3.4501431 |
| C | -1.5628435 | 0.8987222 | -3.5277301 |
| C | -3.2797023 | -0.6111877 | -3.3799025 |
| H | -0.3469122 | 1.4972348 | 3.6306523 |
| H | -4.0126690 | -0.7985525 | 3.3492190 |
| H | 0.3150679 | -1.0833794 | 3.3209459 |
| H | -1.9839511 | -2.5065232 | 3.1432164 |
| H | 0.0449989 | -0.6567585 | -3.6064022 |
| H | -1.9581343 | -2.4112350 | -3.4299681 |
| H | -1.0185752 | 1.8229196 | -3.6230455 |
| H | -4.2666351 | -1.0367798 | -3.2960668 |
| C | 2.3659269 | 2.7863044 | -0.8746113 |
| H | 3.2355333 | 2.1598446 | -0.7615033 |
| C | 0.3385859 | 3.5885980 | -1.5899960 |
| C | 2.0917175 | 3.9871661 | -0.1660580 |
| C | 1.2873579 | 2.5446118 | -1.7594029 |
| C | 0.8456910 | 4.4845548 | -0.6150223 |
| C | 3.2623144 | -2.6412259 | 0.6602222 |
| C | 1.2894261 | -3.3321555 | 1.6025538 |
| C | 1.6897684 | -4.3122940 | 0.6597441 |
| H | 1.1526818 | -5.2143839 | 0.4196337 |
| C | 2.9095814 | -3.8830151 | 0.0736711 |
| H | 3.4562239 | -4.3987489 | -0.6985052 |
| C | 2.2618443 | -2.2962078 | 1.5999414 |
| H | -0.5843844 | 3.7163352 | -2.1295165 |
| H | 2.7081030 | 4.4248992 | 0.6012065 |
| H | 1.2290215 | 1.7158777 | -2.4431866 |
| H | 0.3520904 | 5.3722762 | -0.2600515 |
| H | 4.1292556 | -2.0473516 | 0.4234642 |
| H | 0.4104212 | -3.3857283 | 2.2221379 |
| H | 2.2605700 | -1.4013077 | 2.1999488 |

**Table S 12** Cartesian coordinates of the optimized geometry of [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) in unrestricted singlet spin state at the TPSSH/def2-TZVP level. Total energy = −4750.72882957214 a.u.; <S*S> = 0.0

| | | | |
|---|---|---|---|
| Mo | -1.6257568 | 0.0099527 | 1.4369618 |
| Mo | -1.6023113 | 0.0535813 | -1.2962978 |
| Mo | 0.1906331 | 2.2418105 | 0.2623694 |
| Mo | 1.1656095 | -2.2557295 | -0.6051073 |
| P | -2.1075735 | 1.9343571 | 0.0925872 |
| P | 0.4485644 | -0.0918266 | 0.1204448 |
| P | -1.1489495 | -1.9721357 | 0.0475011 |
| I | -3.9327857 | 3.5285472 | -0.1134486 |
| I | -2.6354223 | -4.0093612 | 0.2084259 |
| I | -4.0211804 | -0.4969568 | 0.0598709 |
| I | -0.6874696 | 4.0720176 | 2.3018461 |
| I | 0.3933105 | -3.9491526 | -2.6529677 |
| I | 2.8215368 | -1.0398541 | -2.5088645 |
| I | 2.1983171 | 1.7945724 | 2.3493508 |
| I | 5.1210408 | 0.8936808 | 1.4250446 |
| I | 7.6936304 | 0.1004263 | 0.7693664 |
| C | -0.9895012 | 0.7432445 | 3.5331240 |
| C | -2.8301227 | -0.6117381 | 3.3595692 |
| C | -0.5346213 | -0.6013199 | 3.3893906 |
| C | -2.4106110 | 0.7366512 | 3.5120442 |
| H | -3.0470893 | 1.6036890 | 3.5937164 |
| C | -1.6790679 | -1.4396082 | 3.2874309 |
| C | -0.7867873 | -0.5948939 | -3.3819792 |
| C | -2.4177004 | 1.0366052 | -3.2726562 |
| H | -2.9219184 | 1.9910383 | -3.2713542 |
| C | -2.0449282 | -1.2380626 | -3.1904103 |
| C | -1.0214064 | 0.8055158 | -3.4280232 |
| C | -3.0430967 | -0.2310359 | -3.1498042 |
| H | -0.3703064 | 1.6143831 | 3.6654092 |
| H | -3.8498796 | -0.9566927 | 3.2875441 |
| H | 0.4969192 | -0.9112232 | 3.4096142 |
| H | -1.6955074 | -2.5121488 | 3.1663010 |
| H | 0.1656244 | -1.0863650 | -3.5055604 |
| H | -2.1963996 | -2.3033694 | -3.1075326 |
| H | -0.2750743 | 1.5546033 | -3.6271377 |
| H | -4.0999437 | -0.3960492 | -3.0139276 |
| C | 2.1902460 | 2.8787384 | -0.8277494 |
| H | 3.1233438 | 2.3927953 | -0.5861403 |
| C | 0.1546833 | 3.3360536 | -1.7873766 |
| C | 1.6453768 | 4.0307930 | -0.1934973 |
| C | 1.2682259 | 2.4365278 | -1.7978782 |
| C | 0.4023819 | 4.3285327 | -0.8129408 |
| C | 3.2322964 | -2.6920203 | 0.4081860 |
| C | 1.2737423 | -3.0953586 | 1.5323652 |
| C | 1.4403352 | -4.1414633 | 0.5782238 |
| H | 0.7749698 | -4.9749550 | 0.4239198 |
| C | 2.6690332 | -3.8857346 | -0.1185927 |
| H | 3.0802665 | -4.4778889 | -0.9192594 |
| C | 2.3747967 | -2.2047831 | 1.4209102 |
| H | -0.7164848 | 3.2962777 | -2.4189224 |
| H | 2.0863609 | 4.5722836 | 0.6276517 |
| H | 1.4184021 | 1.5650053 | -2.4157116 |
| H | -0.2618767 | 5.1342363 | -0.5461816 |
| H | 4.1348791 | -2.2092349 | 0.0717396 |
| H | 0.4553279 | -3.0108230 | 2.2263700 |
| H | 2.5339183 | -1.2961351 | 1.9820424 |

**Table S 13** Cartesian coordinates of the optimized geometry of [(CpMo)$_4$($\mu_4$-P)($\mu_3$-PI)$_2$($\mu$-I)(I)$_3$(I$_3$)] (**2**) in triplet spin state at the TPSSH/def2-TZVP level. Total energy = −4750.73127866544 a.u.; <S*S> = 2.02

| | | | |
|---|---|---|---|
| Mo | -1.6481330 | 0.0542107 | 1.3870333 |
| Mo | -1.7276530 | 0.1869141 | -1.3313277 |
| Mo | 0.1802709 | 2.2316332 | 0.2120354 |
| Mo | 1.2703906 | -2.3698509 | -0.4970123 |
| P | -2.1458332 | 2.0222490 | 0.1137708 |
| P | 0.3582349 | -0.1041762 | -0.0459811 |
| P | -1.1884778 | -1.8660639 | -0.0735995 |
| I | -3.9212410 | 3.6885276 | 0.0754431 |
| I | -2.6551271 | -3.9373907 | 0.0769043 |
| I | -4.0892587 | -0.4137777 | 0.0686528 |
| I | -0.5686997 | 4.0373429 | 2.3310296 |
| I | 0.4777534 | -3.9621855 | -2.5752080 |
| I | 2.9354462 | -0.9805818 | -2.2164297 |
| I | 2.2373209 | 1.6557879 | 2.2187025 |
| I | 5.1971588 | 0.9877866 | 1.2252607 |
| I | 7.8142072 | 0.4439063 | 0.4936693 |
| C | -0.9342585 | 0.7078197 | 3.4906433 |
| C | -2.8463150 | -0.5448700 | 3.3252347 |
| C | -0.5539452 | -0.6524328 | 3.3019279 |
| C | -2.3543346 | 0.7746433 | 3.4995323 |
| H | -2.9424969 | 1.6716023 | 3.6141339 |
| C | -1.7421285 | -1.4289626 | 3.2015180 |
| C | -0.7743375 | -0.3948929 | -3.3784653 |
| C | -2.6010442 | 1.0251602 | -3.3494068 |
| H | -3.2156909 | 1.9117837 | -3.3765122 |
| C | -1.9463308 | -1.1845647 | -3.2304718 |
| C | -1.1849775 | 0.9685338 | -3.4583457 |
| C | -3.0642265 | -0.3092029 | -3.2108216 |
| H | -0.2690096 | 1.5423986 | 3.6335802 |
| H | -3.8844465 | -0.8327780 | 3.2679467 |
| H | 0.4592407 | -1.0157975 | 3.2853534 |
| H | -1.8161216 | -2.4947638 | 3.0480563 |
| H | 0.2363401 | -0.7704400 | -3.4442713 |
| H | -1.9730075 | -2.2595627 | -3.1433855 |
| H | -0.5406048 | 1.8086905 | -3.6491520 |
| H | -4.0934104 | -0.6101930 | -3.0952276 |
| C | 2.1500155 | 2.8281332 | -0.9367423 |
| H | 3.0645125 | 2.2821092 | -0.7612616 |
| C | 0.1004125 | 3.4409814 | -1.7792651 |
| C | 1.6987442 | 3.9768919 | -0.2283524 |
| C | 1.1607661 | 2.4851601 | -1.8824469 |
| C | 0.4489380 | 4.3702783 | -0.7754247 |
| C | 3.2821345 | -2.8301358 | 0.6599791 |
| C | 1.2553079 | -3.3074700 | 1.6312045 |
| C | 1.5490361 | -4.3412544 | 0.7024827 |
| H | 0.9198206 | -5.1881519 | 0.4784413 |
| C | 2.8065729 | -4.0443489 | 0.1014154 |
| H | 3.2936967 | -4.6247714 | -0.6663761 |
| C | 2.3251552 | -2.3678185 | 1.6000714 |
| H | -0.8026032 | 3.4759013 | -2.3651228 |
| H | 2.2047448 | 4.4542398 | 0.5950885 |
| H | 1.2328057 | 1.6442604 | -2.5515164 |
| H | -0.1565342 | 5.1968400 | -0.4417189 |
| H | 4.1967079 | -2.3215055 | 0.3993246 |
| H | 0.3742439 | -3.2579298 | 2.2500764 |
| H | 2.4102690 | -1.4579124 | 2.1753332 |

**Table S 14** Cartesian coordinates of the optimized geometry of [$(CpMo)_4(\mu_4\text{-}P)(\mu_3\text{-}PI)_2(\mu\text{-}I)(I)_3(I_3)$] (**2**) in quintet spin state at the TPSSH/def2-TZVP level. Total energy = −4750.71139308007 a.u.; <S*S> = 6.06

| | | | |
|---|---|---|---|
| Mo | -1.7353693 | 0.0391615 | 1.3563599 |
| Mo | -1.9945103 | -0.0603500 | -1.4083787 |
| Mo | 0.4169338 | 2.3666612 | 0.4563908 |
| Mo | 1.2171747 | -2.2884082 | -0.5484532 |
| P | -1.8856872 | 1.9604278 | -0.0762796 |
| P | 0.2014738 | 0.0030827 | -0.1569926 |
| P | -1.2141682 | -1.9237072 | -0.0170473 |
| I | -3.5539215 | 3.7277516 | -0.4034948 |
| I | -2.6399964 | -3.9875566 | 0.2351396 |
| I | -4.2537186 | -0.3491550 | 0.1392689 |
| I | -0.5692949 | 4.1078284 | 2.4131827 |
| I | 0.4188339 | -3.9872194 | -2.5496165 |
| I | 2.8162362 | -0.9415315 | -2.3663535 |
| I | 2.3024335 | 1.5965051 | 2.4494854 |
| I | 5.2921244 | 1.0488741 | 1.3919810 |
| I | 7.8820589 | 0.5614794 | 0.5660960 |
| C | -1.0085990 | 0.7238388 | 3.4432770 |
| C | -2.9035783 | -0.5600858 | 3.3154527 |
| C | -0.6120291 | -0.6348766 | 3.2612614 |
| C | -2.4303229 | 0.7723301 | 3.4589715 |
| H | -3.0314562 | 1.6604539 | 3.5737050 |
| C | -1.7900638 | -1.4286956 | 3.1964596 |
| C | -0.9628887 | -0.5108694 | -3.4651775 |
| C | -2.8574237 | 0.8028442 | -3.4067501 |
| H | -3.5138411 | 1.6597645 | -3.3841631 |
| C | -2.0896137 | -1.3692204 | -3.3708960 |
| C | -1.4384043 | 0.8321617 | -3.4927474 |
| C | -3.2546016 | -0.5599558 | -3.3292732 |
| H | -0.3535151 | 1.5655033 | 3.5873895 |
| H | -3.9374640 | -0.8653320 | 3.2757577 |
| H | 0.4052042 | -0.9861381 | 3.2440216 |
| H | -1.8491900 | -2.4978155 | 3.0596964 |
| H | 0.0690826 | -0.8282216 | -3.5100222 |
| H | -2.0496885 | -2.4461291 | -3.3156115 |
| H | -0.8329438 | 1.7172580 | -3.6009762 |
| H | -4.2686730 | -0.9178382 | -3.2382565 |
| C | 2.3260864 | 2.7619006 | -0.8030441 |
| H | 3.1998849 | 2.1429874 | -0.6649754 |
| C | 0.2972589 | 3.5338491 | -1.5614530 |
| C | 2.0219367 | 3.9650786 | -0.1051638 |
| C | 1.2646150 | 2.5007655 | -1.7076057 |
| C | 0.7742552 | 4.4426780 | -0.5800848 |
| C | 3.2661988 | -2.6326301 | 0.5795947 |
| C | 1.2883779 | -3.2299888 | 1.5819279 |
| C | 1.6289668 | -4.2445662 | 0.6478940 |
| H | 1.0477101 | -5.1271752 | 0.4331075 |
| C | 2.8543382 | -3.8734370 | 0.0260088 |
| H | 3.3611745 | -4.4229370 | -0.7516950 |
| C | 2.2990613 | -2.2290900 | 1.5349278 |
| H | -0.6228703 | 3.6420799 | -2.1132168 |
| H | 2.6143260 | 4.4119419 | 0.6773636 |
| H | 1.2266503 | 1.6582974 | -2.3793531 |
| H | 0.2574725 | 5.3222624 | -0.2340512 |
| H | 4.1468654 | -2.0729250 | 0.3076998 |
| H | 0.4174756 | -3.2346601 | 2.2170169 |
| H | 2.3396231 | -1.3172516 | 2.111694 |

## [{CpMo(CO)$_2$}$_2$(μ-PBr$_2$)$_2$] (3a)

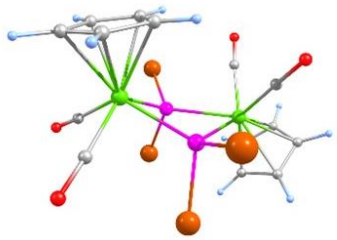

**Table S 15** Cartesian coordinates of the optimized geometry of [{CpMo(CO)$_2$}$_2$(μ-PBr$_2$)$_2$] (**3a**) at the B3LYP/def2-TZVP level. Total energy = −11957.0057876 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo | 1.669991000 | 0.925554000 | 0.314907000 | H | -2.456602000 | 1.835793000 | -0.737011000 |
| Mo | -1.821006000 | -1.217612000 | -0.419170000 | C | 3.669434000 | -0.252304000 | -0.129815000 |
| P | 0.230863000 | -1.037250000 | 1.034651000 | H | 3.635029000 | -1.264665000 | -0.493467000 |
| P | 0.202763000 | -0.135493000 | -1.463316000 | C | -1.785561000 | -2.241140000 | -2.126073000 |
| Br | 1.506994000 | -1.530860000 | -2.740360000 | C | -4.135279000 | -1.023844000 | -0.322259000 |
| Br | 1.549538000 | -2.917483000 | 1.101113000 | H | -4.774555000 | -1.842269000 | -0.609708000 |
| Br | -0.390870000 | -1.108303000 | 3.251497000 | C | 3.765476000 | 1.562207000 | 1.274110000 |
| Br | -0.463626000 | 1.219981000 | -3.202396000 | H | 3.811456000 | 2.170039000 | 2.163532000 |
| O | -1.837103000 | -2.834346000 | -3.104471000 | C | 3.716550000 | 0.144739000 | 1.234940000 |
| O | 0.317001000 | 2.229642000 | 2.816209000 | H | 3.724188000 | -0.515035000 | 2.087051000 |
| O | 0.281181000 | 3.517568000 | -0.753382000 | C | 3.694109000 | 0.923032000 | -0.929829000 |
| O | -1.796125000 | -4.176514000 | 0.614802000 | H | 3.681431000 | 0.956948000 | -2.006926000 |
| C | 0.776918000 | 1.704248000 | 1.904665000 | C | 3.751559000 | 2.041264000 | -0.058383000 |
| C | -1.759461000 | -3.094927000 | 0.239781000 | H | 3.785171000 | 3.076549000 | -0.357890000 |
| C | -3.673216000 | 0.020840000 | -1.174136000 | C | -2.910087000 | 0.453408000 | 0.946979000 |
| H | -3.883868000 | 0.126408000 | -2.225667000 | H | -2.426957000 | 0.926515000 | 1.786170000 |
| C | 0.753787000 | 2.534245000 | -0.395461000 | C | -3.647700000 | -0.759267000 | 0.990330000 |
| C | -2.925781000 | 0.932599000 | -0.382611000 | H | -3.835639000 | -1.350267000 | 1.871594000 |

## [{CpMo(CO)$_2$}(CpMoBr$_2$)(μ-PBr$_2$)$_2$] (4a)

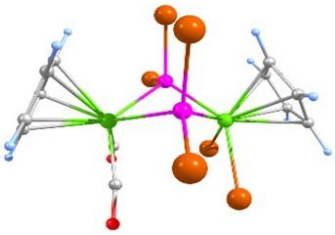

**Table S 16** Cartesian coordinates of the optimized geometry of [{CpMo(CO)$_2$}(CpMoBr$_2$)(μ-PBr$_2$)$_2$] (**4a**) at the B3LYP/def2-TZVP level. Total energy = −16878.6432952 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo | 1.580869000 | -0.180774000 | 1.008034000 | H | 0.801225000 | -0.895987000 | 3.826413000 |
| Mo | -0.887202000 | -0.362220000 | -1.361319000 | C | 2.364305000 | 1.602851000 | 2.249601000 |
| Br | -1.406746000 | -3.003533000 | 1.649350000 | H | 2.480535000 | 2.578775000 | 1.809292000 |
| Br | 1.453277000 | 2.900682000 | -1.784005000 | C | 3.379391000 | 0.612722000 | 2.352954000 |
| Br | -0.763435000 | 3.105064000 | 0.734599000 | H | 4.371037000 | 0.682800000 | 1.941999000 |
| Br | -2.185491000 | 0.167680000 | 2.444282000 | C | 1.185710000 | 1.088589000 | 2.864665000 |
| Br | 2.123513000 | -2.727239000 | 0.796309000 | H | 0.260668000 | 1.617130000 | 3.005041000 |
| Br | 3.455928000 | 0.021625000 | -0.799831000 | C | -2.158015000 | 0.757134000 | -2.976827000 |
| P | 0.450079000 | 1.478737000 | -0.310005000 | H | -1.697389000 | 1.382665000 | -3.724011000 |
| P | -0.707334000 | -0.909154000 | 1.078482000 | C | -3.221965000 | 0.075675000 | -1.059496000 |
| O | 1.366243000 | -0.266272000 | -3.567473000 | H | -3.683742000 | 0.089486000 | -0.086398000 |
| O | -0.165244000 | -3.410229000 | -1.738114000 | C | -2.671050000 | 1.194854000 | -1.729420000 |
| C | 0.634041000 | -0.266082000 | -2.697360000 | H | -2.642671000 | 2.203134000 | -1.351321000 |
| C | -0.364147000 | -2.315050000 | -1.505168000 | C | -3.054538000 | -1.063869000 | -1.887419000 |
| C | 2.836975000 | -0.509706000 | 3.004394000 | H | -3.394216000 | -2.061932000 | -1.663459000 |
| H | 3.343776000 | -1.442960000 | 3.175741000 | C | -2.394958000 | -0.645777000 | -3.081706000 |
| C | 1.477460000 | -0.232143000 | 3.314717000 | H | -2.166889000 | -1.266676000 | -3.932540000 |

## [{CpMo(CO)$_2$}$_2$(μ-PCl$_2$)$_2$] (3b)

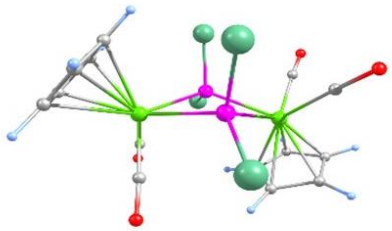

**Table S 17** Cartesian coordinates of the optimized geometry of [{CpMo(CO)$_2$}$_2$(μ-PCl$_2$)$_2$] (**3b**) at the B3LYP/def2-TZVP level. Total energy = −3501.1892496 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo | 1.722110000 | 0.847759000 | 0.286562000 | H | -2.421916000 | 1.748473000 | -0.768963000 |
| Mo | -1.752180000 | -1.297647000 | -0.448598000 | C | 3.693014000 | -0.370517000 | -0.173489000 |
| P | 0.282843000 | -1.097346000 | 1.011271000 | H | 3.636108000 | -1.382143000 | -0.536749000 |
| P | 0.255164000 | -0.197266000 | -1.484264000 | C | -1.673728000 | -2.319892000 | -2.153672000 |
| Cl | 1.458701000 | -1.470767000 | -2.656803000 | C | -4.072283000 | -1.129011000 | -0.362298000 |
| Cl | 1.499978000 | -2.817597000 | 1.077656000 | H | -4.703039000 | -1.953047000 | -0.652469000 |
| Cl | -0.288390000 | -1.142462000 | 3.042501000 | C | 3.839635000 | 1.441712000 | 1.229178000 |
| Cl | -0.356051000 | 1.060066000 | -3.065310000 | H | 3.906355000 | 2.048544000 | 2.117953000 |
| O | -1.694886000 | -2.913775000 | -3.133428000 | C | 3.760071000 | 0.025511000 | 1.190839000 |
| O | 0.369866000 | 2.132530000 | 2.800420000 | H | 3.762834000 | -0.634367000 | 2.042898000 |
| O | 0.330413000 | 3.431883000 | -0.801708000 | C | 3.736426000 | 0.804167000 | -0.974015000 |
| O | -1.654351000 | -4.254551000 | 0.586167000 | H | 3.717915000 | 0.838137000 | -2.051027000 |
| C | 0.832941000 | 1.621783000 | 1.881792000 | C | 3.825068000 | 1.920909000 | -0.103180000 |
| C | -1.647955000 | -3.172060000 | 0.210362000 | H | 3.878731000 | 2.955241000 | -0.403012000 |
| C | -3.617602000 | -0.079047000 | -1.211652000 | C | -2.867221000 | 0.359786000 | 0.912851000 |
| H | -3.826494000 | 0.025067000 | -2.263711000 | H | -2.394181000 | 0.838564000 | 1.754706000 |
| C | 0.807624000 | 2.455582000 | -0.429861000 | C | -3.593824000 | -0.859355000 | 0.952598000 |
| C | -2.881829000 | 0.839349000 | -0.417266000 | H | -3.781485000 | -1.451956000 | 1.83288900 |

## [{CpMo(CO)$_2$}(CpMoCl$_2$)(μ-PCl$_2$)$_2$] (4b)

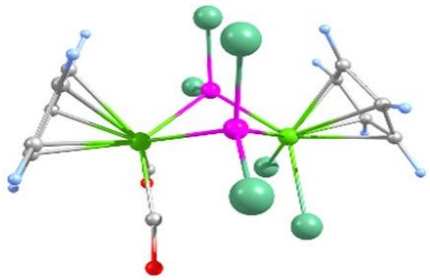

**Table S 18** *:* Cartesian coordinates of the optimized geometry of [{CpMo(CO)$_2$}(CpMoCl$_2$)(μ-PCl$_2$)$_2$] (**4b**) at the B3LYP/def2-TZVP level. Total energy = −4194.9156358a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mo | 1.576536000 | -0.185980000 | 0.995818000 | H | 0.790830000 | -0.896154000 | 3.818728000 |
| Mo | -0.882979000 | -0.366544000 | -1.366258000 | C | 2.353926000 | 1.601003000 | 2.235104000 |
| Cl | -1.313128000 | -2.817857000 | 1.618626000 | H | 2.474137000 | 2.578252000 | 1.799055000 |
| Cl | -2.058033000 | 0.120921000 | 2.288795000 | C | 3.366987000 | 0.608318000 | 2.337562000 |
| Cl | -0.699806000 | 2.925185000 | 0.656996000 | H | 4.354305000 | 0.671539000 | 1.913795000 |
| Cl | 1.396411000 | 2.770666000 | -1.628948000 | C | 1.172870000 | 1.086505000 | 2.848077000 |
| Cl | 2.052257000 | -2.572825000 | 0.767525000 | H | 0.247699000 | 1.615662000 | 2.987252000 |
| Cl | 3.299704000 | -0.000096000 | -0.728137000 | C | -2.164087000 | 0.764369000 | -2.967653000 |
| P | 0.448483000 | 1.464875000 | -0.309134000 | H | -1.708397000 | 1.391104000 | -3.716810000 |
| P | -0.699796000 | -0.903148000 | 1.067563000 | C | -3.212705000 | 0.079280000 | -1.043436000 |
| O | 1.417490000 | -0.239015000 | -3.524519000 | H | -3.666233000 | 0.091785000 | -0.066410000 |
| O | -0.126666000 | -3.415628000 | -1.675585000 | C | -2.663247000 | 1.198912000 | -1.713366000 |
| C | 0.659257000 | -0.259335000 | -2.677114000 | H | -2.628357000 | 2.205448000 | -1.331065000 |
| C | -0.340507000 | -2.315833000 | -1.480130000 | C | -3.058464000 | -1.057136000 | -1.878503000 |
| C | 2.823814000 | -0.512846000 | 2.989265000 | H | -3.401621000 | -2.054460000 | -1.656665000 |
| H | 3.325702000 | -1.451616000 | 3.147984000 | C | -2.409486000 | -0.636506000 | -3.077411000 |
| C | 1.464808000 | -0.234173000 | 3.301881000 | H | -2.191705000 | -1.254673000 | -3.932881000 |

References:


(1) Scherer, O.J.; Sitzmann, H.; Wolmershäuser, G., Umsetzung von $P_4$ mit ($\eta^5$-$C_5H_5$)$(CO)_2$Mo≡Mo$(CO)_2$($\eta^5$-$C_5H_5$) zu den tetraedrischen Molybdänkomplexen $P_n$[Mo$(CO)_2$($\eta^5$-$C_5H_5$)]$_{4-n}$ (*n* = 2,3). *J. Organomet. Chem.* **1984**, *268*, C9-C12.

(2) CrysAlisPro Software System, Rigaku Oxford Diffraction, **2020**.

(3) CrysAlisPro Software System, Rigaku Oxford Diffraction, **2015**.

(4) CrysAlisPro Software System, Rigaku Oxford Diffraction, **2017**.

(5) Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. Olex2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(6) Sheldrick, G.M. ShelXT-Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.

(7) Sheldrick, G.M. Crystal structure refinement with ShelXL. *Acta Cryst.* **2015**, *C71*, 3-8.

([8]) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* **1989**, *162*, 165–169.

([9]) Treutler, O.; Ahlrichs, R. Efficient molecular numerical integration schemes. *J. Chem. Phys.* **1995**, *102*, 346–354.

([10]) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, **1988**, *38*, 3098.

([11]) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, *33*, 8822-8824; Erratum: Perdew, J. *P. Phys. Rev. B* **1986**, *34*, 7406.

([12]) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* **1993**, *98*, 5648-5652.

([13]) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785-789.

([14]) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868; Erratum *Phys. Rev. Lett.* **1997**, *78*, 1396.

([15]) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982-9985.

([16]) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787-1799.
([17]) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
([18]) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003**, *119*, 12129-12137.
([19]) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829.
([20]) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theor. Chem. Acc.* **1997**, *97*, 119.
([21]) Eichkorn, K.; Treutler, O.; Oehm, H.; Häser, M.; Ahlrichs, R. Auxiliary basis sets to approximate Coulomb potentials. *Chem. Phys. Lett.* **1995**, *242*, 652–660.
([22]) Sierka, M.; Hogekamp, A.; Ahlrichs, R. Fast evaluation of the Coulomb potential for electron densities using multipole accelerated resolution of identity approximation. *J. Chem. Phys.* **2003**, *118*, 9136.
(23) Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. ; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V; Cioslowski, J.; Fox, D. J. *Gaussian, Inc*., Wallingford CT, **2013**.