Preorganized Ag\textsuperscript{I} Bimetallic Precursor with Labile Diphosphorus Ligands for a Programmed Synthesis of Organometallic–Organic Hybrid Polymers

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Methods

All manipulations were carried out under an inert atmosphere of dried nitrogen using standard Schlenk techniques. The Ag¹ salt Ag[BF₄] 2 and the organic linkers 4,4' -bipyridine (6), trans-1,2-Di(4-pyridyl)ethylene (7) and 1,2-Bis(4-pyridyl)ethane (8) were purchased from Sigma-Aldrich and used as received. The ligand complex [Cp₂Mo₂(CO)₄P₂] (1) was prepared according to literature procedure.[¹] Solvents were freshly distilled under argon from Na/K alloy (n-pentane) or from CaH₂ (CH₂Cl₂ and CH₃CN). IR spectra were recorded as KBr discs on varian FTS-800 spectrometer. ¹H, ¹³C, ³¹P and ¹⁹F spectra were recorded on a Bruker Avance 300 spectrometer. ¹H and ¹³C, ³¹P and ¹⁹F NMR chemical shifts were reported in parts per million (ppm) relative to external standard Me₄Si, H₃PO₄ (85%) or CFCl₃. Elemental analysis were performed by the microanalytical laboratory of the Universität Regensburg. For the ESI-MS a Finnigan ThermoQuest TSQ 7000 mass spectrometer was used.

General Procedure:

In a Schlenk-tube, one equivalent of Ag[BF₄] (2, 10 mg, 0.05 mmol) and two equivalents of Mo₂P₂ (1, 50 mg, 0.10 mmol) were dissolved in dichloromethane (8 mL) and stirred for 1h at room temperature during which the Ag¹ dimer 3 precipitated as an orange powder in quantitative yield. To the crude mixture was added acetonitrile (3 ml) to dissolve the dimer 3 and subsequently one (in the case of polymers 9-11) or two (in the case of polymers 12-14) equivalent of the organic linkers (6-8) in a mixture of (dichloromethane : acetonitrile; 4 ml : 1 ml) were added. The whole mixture was stirred for further 2h at room temperature, filtered and carefully layered with 15 ml of n-pentane. In few days orange or red crystals of 9-14 are obtained, collected, washed with n-pentane (5 ml × 2) and dried in vacuum.
Synthesis of [(Cp₂Mo₂(CO)₆(μ₆-N)⁰₁:²:²-P₃)]₂{(Cp₂Mo₂(CO)₆(μ₆-N)⁰₁:²:²-P₃)}₂{(μ₆-N)⁰₁:²:²-C₈H₈N₂}Ag₂][BF₄]₂n (9):

Following the general procedure, the reaction of bipy (6; 4 mg, 0.025 mmol) and the dimer 3 (60 mg, 0.025 mmol) in a mixture of dichloromethane (12 ml) and acetonitrile (4 ml) afforded after crystallization the compound 9 x 3-CH₂Cl₂ x 3-CH₃CN as a crystalline orange solid (49 mg, yield 77%). ¹H NMR (300 MHz, CD₃CN): δ = 5.37 (s, 40H, C₅H₅), 7.69 (m, 4H; CH(bpy)), 8.71 ppm (m, 4H; CH(bpy)). ¹³C{¹H} NMR (75.47 MHz, CD₃CN): δ = 88.0 (s, C₅H₅), 122.6 (s, CH(bpy)), 146.3 (s, CH(bpy)), 151.7 (s, C(bpy)), 225.0 ppm (s, CO). ³¹P{¹H} NMR (121.49 MHz, CD₃CN): δ = -71.6 (s) ppm. ¹⁹F{¹H} NMR (282.40 MHz, CD₃CN): δ = -150.5 (s; ¹¹BF₄), -150.5 ppm (s; ¹⁰BF₄). ESI-MS (CH₃CN), Cations: m/z (%) = 1790.8 (1) [Ag₂{(Cp₂Mo₂(CO)₆P₃)₂}⁺], 1100.6 (100) [Ag{(Cp₂Mo₂(CO)₆P₃)₂}⁺], 599.8 (60) [Ag{(Cp₂Mo₂(CO)₆P₃)₂}⁺], 571.8 (10) [Ag{(Cp₂Mo₂(CO)₆P₃)₂}⁺] - CO), 543.7 (13) [Ag{(Cp₂Mo₂(CO)₆P₃)₂}⁺] - 2 CO), 517.7 (6) [Ag{(Cp₂Mo₂(CO)₆P₃)₂}⁺] - 3 CO), 495.7 (22) [%{(Cp₂Mo₂(CO)₆P₃)₂}⁺], 439.8 (13) [%{(Cp₂Mo₂(CO)₆P₃)₂}⁺] - 2 CO). IR (KBr): ε/cm⁻¹ = 3115 (w), 2963 (vw), 1946 (vs, CO), 1912 (vs; CO), 1635 (w), 1599 (w), 1420 (w), 1358 (vw), 1262 (w), 1084 (m), 1049 (m), 1013 (m), 818 (m), 669 (vw), 616 (vw), 562 (w), 521 (m), 492 (w), 455 (m). Elemental analysis, calcd. (%) for C₃₃H₂₆AgBF₄Mo₆NO₃P₄ (1271.57 g·mol⁻¹): C 31.14, H 1.90, N 1.10; found: C 30.87, H 1.89. N 1.04.

Synthesis of [(Cp₂Mo₂(CO)₆(μ₆-N)⁰₁:²:²-P₃)]₂{(Cp₂Mo₂(CO)₆(μ₆-N)⁰₁:²:²-P₃)}₂{(μ₆-N)⁰₁:²:²-C₁₂H₁₀N₂}Ag₂][BF₄]₂n (10):

Following the general procedure, the reaction of dpe (7; 5 mg, 0.025 mmol) and the dimer 3 (60 mg, 0.025 mmol) in a mixture of dichloromethane (12 ml) and acetonitrile (4 ml) afforded after crystallization the polymer 10 x 2•CH₂Cl₂ as a crystalline orange solid (40 mg, yield 56%). ¹H NMR (300 MHz, CD₃CN): δ = 5.36 (s, 40H, C₅H₅), 7.41 (s, 2H; CH(dpe)), 7.52 (m, 4H; CH(dpe)), 8.58 ppm (m, 4H; CH(dpe)). ¹³C{¹H} NMR (75.47 MHz, CD₃CN): δ = 87.8 (s, C₅H₅), 122.4 (s,
CH$_{3}$dpe), 131.7 (s, CH$_{3}$dpe), 151.1 (s, C$_{dpe}$), 225.7 ppm (s, CO). $^{31}$P($^1$H) NMR (121.49 MHz, CD$_3$CN): $\delta$ = -64.2 (br s) ppm. $^{19}$F($^1$H) NMR (282.40 MHz, CD$_3$CN): $\delta$ = -150.5 (s; $^{11}$BF$_4$), -150.4 ppm (s; $^{10}$BF$_4$). ESI-MS (CH$_3$CN), Cations: m/z (%) = 1791.7 (100) [Ag$_2$(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_3$(BF$_4$)]*; 1100.7 (100) [Ag(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_2$]*, 643.8 (78) [Ag(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_2$(CH$_3$CN)]*. IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3113 (w), 2962 (vw), 2924 (w), 2853 (w), 2016 (m), 1948 (vs, CO), 1914 (vs; CO), 1604 (m), 1466 (w), 1421 (w), 1356 (vv, 1262 (m), 1084 (s), 1034 (m), 1010 (m), 920 (w), 864 (w), 822 (m), 676 (vv), 563 (w), 518 (m), 485 (m), 457 (m). Elemental analysis, calcd. (%) for C$_9$H$_{12}$AgBF$_4$Mo$_4$NO$_4$P$_4$: 31.96, H 1.97, N 1.10; found: C 32.10, H 2.16, N 1.51.

Synthesis of [{Cp$_2$Mo$_2$(CO)$_4$($\mu_4$$_{1:1:2:2}$-P$_2$)$_3$}[Cp$_2$Mo$_2$(CO)$_4$($\mu_5$$_{1:1:2:2}$-P$_3$)$_2$]{$\mu_4$$_{1:1}$-C$_{12}$H$_{12}$N$_2$]Ag$_2$]$_n$[BF$_4$]$_{2n}$ (11):

Following the general procedure, the reaction of bpe (8; 5 mg, 0.025 mmol) and the dimer 3 (60 mg, 0.025 mmol) in a mixture of dichloromethane (12 ml) and acetonitrile (4 ml) afforded after crystallization the compound 9 x 2CH$_2$Cl$_2$ as a crystalline orange solid (41 mg, yield 64%). $^1$H NMR (300 MHz, CD$_3$CN): $\delta$ = 3.01 (s, 4H, CH$_2$(bpe), 5.37 (s, 40H, C$_3$H$_5$), 7.56 (m, 4H, CH$_3$(bpe)), 8.58 ppm (m, 4H, CH$_{3}$bpe)). $^{13}$C($^1$H) NMR (75.47 MHz, CD$_3$CN): $\delta$ = 34.8 (s, CH$_2$(bpe)), 86.4 (s, C$_3$H$_5$), 124.7 (s, CH$_3$(bpe)), 149.1 (s, CH$_3$(bpe)), 152.2 (s, C$_3$(bpe)), 225.1 ppm (s, CO). $^{31}$P($^1$H) NMR (121.49 MHz, CD$_3$CN): $\delta$ = -69.3 (s) ppm. $^{19}$F($^1$H) NMR (121.49 MHz, CD$_3$CN): $\delta$ = -150.5 (s; $^{11}$BF$_4$), -150.5 ppm (s; $^{10}$BF$_4$). ESI-MS (CH$_3$CN), Cations: m/z (%) = 1791.4 (66) [Ag$_2$(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_3$(BF$_4$)]*; 1100.7 (100) [Ag(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_2$]*, 598.6 (81) [Ag(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_2$]*, 572.0 (12) [Ag(Cp$_2$Mo$_2$(CO)$_4$P$_2$)$_2$] - CO, IR (KBr): $\tilde{\nu}$/cm$^{-1}$ = 3113 (w), 2952 (vw), 2925 (w), 2858 (vw), 1969 (vs, CO), 1920 (vs; CO), 1614 (m), 1482 (w), 1422 (w), 1360 (vw), 1262 (w), 1084 (m), 1034 (m), 1008 (m), 920 (w), 825 (m), 679 (vw), 560 (w), 520 (m), 490 (m).
Synthesis of [(Cp₂Mo₂(CO)₆(μ₄-η¹⁻¹⁻₂⁻₂-P₃))₂{μ₁-η¹⁻¹⁻₆⁻⁻₁⁻⁻⁻⁻⁻⁻₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋ профессиональный привет
(w), 870 (vw), 837 (m), 819 (m), 736 (w), 693 (vw), 563 (m), 520 (m), 485 (m), 459 (m). Elemental analysis, calcd. (%) for C_{26}H_{20}AgBF_{4}Mo_{2}N_{2}O_{4}P_{2} (872.94 g·mol^{-1}): C 35.77, H 2.31, N 3.21; found: C 35.62, H 2.56. N 3.71.

**Synthesis of** \([\{Cp_{2}Mo_{2}(CO)_{4}(\mu_{4}η^{1:1:2:2}-P_{3}\})_{2}\{\mu_{2}η^{1:1}-C_{12}H_{12}N_{2}\}_{2}Ag_{3}[BF_{4}]_{2n} (14):}

Following the general procedure, the reaction of bpe (8; 10 mg, 0.050 mmol) and the dimer 3 (60 mg, 0.025 mmol) in a mixture of dichloromethane (12 ml) and acetonitrile (4 ml) afforded after crystallization the compound 14 x 0.5·CH_{2}CN as a crystalline orange solid (20 mg, yield 51%). \(^{1}\text{H} \text{NMR} (300 \text{ MHz, CD}_{2}\text{CN}): \delta = 2.99 (s, 8H, CH}_{2}(bpe)), 5.37 (s, 20H, C_{3}H_{5}), 7.58 (m, 8H; CH_{(bpe)}), 8.64 \text{ ppm} \text{ (m, 8H; CH}_{(bpe)}). \ ^{31}P{^{1}}\text{H} \text{NMR} (121.49 \text{ MHz, CD}_{2}\text{CN}): \delta = -83.3 \text{ ppm}. \ ^{19}F{^{1}}\text{H} \text{NMR} (121.49 \text{ MHz, CD}_{2}\text{CN}): \delta = -150.5 \text{ ppm} {^{11}}\text{BF}_{4}{}, -150.5 \text{ ppm} \text{ (s; }^{10}\text{BF}_{4}). \text{ ESI-MS (CH}_{3}\text{CN), Cations: m/z} \text{ (}\%\text{) = 1790.2 (24)} \text{ [Ag}_{2}(Cp_{2}Mo_{2}(CO)_{4}P_{2})_{3}(BF}_{4})^{{}\text{+}}, 1100.7 (100) \text{ [Ag(Cp}_{2}Mo_{2}(CO)_{4}P_{2})_{3}]^{{}\text{+}} \text{. IR (KBr): }\tilde{\nu}/\text{cm}^{-1} = 3117 \text{ (w), 2960 (vw), 2921 (w), 2851 (w), 1973 (vs, CO), 1922 (vs; CO), 1608 (m), 1499 (w), 1424 (w), 1356 (vw), 1275 (w), 1078 (m), 1050 (m), 1002 (m), 914 (w), 822 (m), 670 (w), 561 (w), 525 (m), 490 (w).} \text{ Elemental analysis, calcd.} \text{ (%) for C}_{26}H_{20}AgBF_{4}Mo_{2}N_{2}O_{4}P_{2} (874.96 g·mol^{-1}): C 35.69, H 2.53, N 3.20; found: C 35.68, H 2.85. N 3.95.

**Crystallographic data**

The crystal samples were processed at Gemini R Ultra (10, 11) and a SuperNova TitanS2 (9, 12, 13, 14) diffractometer, respectively. Frames integration and data reduction were performed with CrysAlisPro ver. 171.38.41h. Analytical absorption corrections from crystal faces was applied to the data of 9, 11 and 12. A numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied to the data of 10, 13 and 14. All structures were solved by ShelXT using Olex2. For all structures a least-square refinement on F^2 was carried out with SHELXL. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. CCDC-1567453 (9), CCDC-1567454 (10), CCDC-1567455 (11), CCDC-1567456 (12), CCDC-1567457 (13), CCDC-1567458 (14) 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](http://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).

**Compound 9:**

The solvent molecules in the asymmetric unit (3 x CH₂Cl₂, 3 x MeCN) were found to be heavily disordered and all attempts to refine distinct positions for these solvent molecules failed. Therefore we applied the solvent mask function of Olex2. We found two voids in the unit cell (see cif). Void 1 with a size of 620.2 Å³ and an electron count of 172.0 and void 2 with a size of 572.1 Å³ and an electron count of 207.1. The electron count of 172.0 (void 1) can be related to one molecule of CH₂Cl₂ and two molecules of MeCN per asymmetric unit. The electron count of 207.1 (void 2) can be related to two molecules of CH₂Cl₂ and one molecule of MeCN per asymmetric unit. Additionally, the structure contains a Ï1 bound [Cp₂Mo₂(CO)₄(η²-P₂)] ligand, which shows a disorder over two positions with a ratio of 82:18. To describe the disordered fragments the restrains DFIX, SADI and SIMU were applied.

**Compound 10:**

All tested crystals of 10 were twinned, therefore a twin refinement with the HKLF5 file was performed (BASF 0.0842). Additionally, the sample was weakly diffracting at higher angles, although Cu-Kα radiation was used. Therefore no reflections above a resolution of 0.87 Å were recorded.

**Compound 13:**

A CH₂Cl₂ molecule was found to be heavily disordered and all attempts to refine distinct positions failed. Therefore we applied the solvent mask function of Olex2. We found a void with a size of 282.9 Å³ and an electron count of 77.8, which can be related to one molecule of CH₂Cl₂ per asymmetric unit. Additionally, a dpe linker molecule shows a disorder over two positions in the ratio 61:39. To describe this disorder the SIMU restrain was applied.
Topological analysis of 2D and 3D coordination polymers 12-14. Topology of the underlying nets in 12-14 was determined using ToposPro program set according to the procedure described in.[7] The classification of the topological types as 3-character symbols hcb (in 12 and 13) and ths (in 14) is given according to the Reticular Chemistry Structure Resource database.[8]

Figure S1. The underlying nets: 2D in 12 (a) and 13 (b), and 3D in 14 (c), an idealized ths net (d). The circles depict Ag atoms. Thin blue and thick red cylinders denote ditopic pyridine-based linkers and [Cp₂Mo₂(CO)₄(n²-P₂)] bridging fragments, respectively.
### Table S1: Crystallographic data of the compounds 9, 10 and 11.

| Compound | 9          | 10          | 11          |
|----------|------------|-------------|-------------|
| Formula  | C_{75}H_{63}Ag_{2}B_{2}Cl_{6}FeMo_{3}N_{5}O_{16}P_{6} | C_{36}H_{52}AgBCl_{4}Mo_{4}NO_{8}P_{4} | C_{36}H_{52}AgBCl_{4}Mo_{4}NO_{8}P_{4} |
| D_{calc} / g cm\(^{-3}\) | 1.975 | 2.049 | 2.059 |
| \(\mu/\text{mm}^2\) | 14.652  | 15.768 | 1.886 |
| Formula Weight | 2907.64 | 1447.72 | 1448.73 |
| Color | orange | orange | orange |
| Shape | block | block | block |
| Size/mm\(^3\) | 0.27\(\times\)0.19\(\times\)0.12 | 0.18\(\times\)0.10\(\times\)0.09 | 0.33\(\times\)0.25\(\times\)0.23 |
| TIK | 123(1) | 123(1) | 123(2) |
| Crystal System | triclinic | triclinic | triclinic |
| Space Group | P-1 | P-1 | P-1 |
| \(a/\text{Å}\) | 13.4948(3) | 11.3648(4) | 11.2781(3) |
| \(b/\text{Å}\) | 15.0279(4) | 13.7705(4) | 13.7599(3) |
| \(c/\text{Å}\) | 27.1364(4) | 15.6583(4) | 15.7450(4) |
| \(\alpha/°\) | 90.123(2) | 104.321(2) | 104.574(2) |
| \(\beta/°\) | 101.940(2) | 90.936(2) | 91.012(2) |
| \(\gamma/°\) | 114.138(2) | 98.281(2) | 98.274(2) |
| V/Å\(^3\) | 4890.1(2) | 2346.15(12) | 2336.46(10) |
| Z | 2 | 2 | 2 |
| Z' | 1 | 1 | 1 |
| \(\Theta_{max}/°\) | 3.238 | 3.352 | 3.326 |
| \(\Theta_{max}/°\) | 74.424 | 66.841 | 32.483 |
| Measured Refl. | 54153 | 8423 | 35809 |
| Independent Refl. | 19226 | 8423 | 15104 |
| Reflections Used | 17469 | 7227 | 12912 |
| \(R_{int}\) | 0.0442 | 0.0632 | 0.0263 |
| Parameters | 1181 | 569 | 568 |
| Restraints | 233 | 0 | 0 |
| Largest Peak | 1.464 | 1.223 | 0.698 |
| Deepest Hole | -1.481 | -1.271 | -0.943 |
| Goof | 1.032 | 1.106 | 1.018 |
| wR\(_2\) (all data) | 0.1024 | 0.1277 | 0.0573 |
| wR\(_2\) | 0.0990 | 0.1222 | 0.0542 |
| R\(_1\) (all data) | 0.0436 | 0.0492 | 0.0354 |
| R\(_1\) | 0.0397 | 0.0427 | 0.0267 |
| Diffractometer | Supernova, TitanS2 | Gemini R Ultra, Ruby | Gemini Ultra, AtlasS2 |
| Radiation (\(\lambda\)) | Cu (1.54184Å) | Cu (1.54184Å) | Mo (0.71073Å) |
| Absorption correction | analytical | gaussian | analytical |
Table S2: Crystallographic data of compounds 12, 13 and 14.

| Compound | 12 | 13 | 14 |
|----------|----|----|----|
| Formula  | C$_{24}$H$_{18}$AgBF$_4$Mo$_2$N$_2$O$_4$P$_2$ | C$_{28}$H$_{24}$AgBCl$_4$F$_4$Mo$_2$N$_2$O$_4$P$_2$ | C$_{27}$H$_{23.5}$AgBF$_4$Mo$_2$N$_{2.5}$O$_4$P$_2$ |
| $D_{calc}$/ g cm$^{-3}$ | 1.996 | 1.820 | 1.946 |
| $\mu$/mm$^{-1}$ | 14.325 | 13.270 | 13.256 |
| Formula Weight | 846.90 | 1042.79 | 895.48 |
| Color | red | orange | orange |
| Shape | block | block | block |
| Size/mm$^3$ | 0.23×0.17×0.10 | 0.46×0.37×0.22 | 0.47×0.23×0.07 |
| Temperature | 123(1) | 123(1) | 123(1) |
| Crystal System | monoclinic | triclinic | monoclinic |
| Space Group | P2$_1$/c | P-1 | C2/c |
| a/Å | 11.0529(3) | 11.3496(3) | 25.7099(7) |
| b/Å | 17.8820(3) | 13.0896(3) | 15.4522(5) |
| c/Å | 15.1557(4) | 14.4870(3) | 15.4089(5) |
| $\alpha$/° | 90 | 114.678(2) | 90 |
| $\beta$/° | 109.809(3) | 101.588(2) | 96.892(3) |
| $\gamma$/° | 90 | 91.143(2) | 90 |
| V/Å$^3$ | 2818.24(13) | 1902.71(8) | 6112.7(3) |
| Z | 4 | 2 | 8 |
| $Z'$ | 1 | 1 | 1 |
| $\Theta_{mof}$/° | 3.965 | 3.450 | 3.329 |
| $\Theta_{max}$/° | 74.250 | 74.403 | 74.369 |
| Measured Refl. | 15615 | 20417 | 14962 |
| Independent Refl. | 5581 | 7451 | 6010 |
| Reflections Used | 5372 | 7086 | 5650 |
| $R_{int}$ | 0.0291 | 0.0501 | 0.0512 |
| Parameters | 361 | 470 | 395 |
| Restraints | 0 | 192 | 0 |
| Largest Peak | 2.248 | 1.405 | 2.286 |
| Deepest Hole | -1.566 | -1.548 | -1.533 |
| GoF | 1.270 | 1.066 | 1.064 |
| wR$_2$ (all data) | 0.1054 | 0.1361 | 0.1690 |
| wR$_1$ | 0.1048 | 0.1343 | 0.1655 |
| R$_1$ (all data) | 0.0500 | 0.0501 | 0.0607 |
| R$_{I}$ | 0.0486 | 0.0488 | 0.0582 |
| Diffractometer | Supernova, TitanS2 | Supernova, TitanS2 | Supernova, TitanS2 |
| Radiation (\(\lambda\)) | Cu (1.54184Å) | Cu (1.54184Å) | Cu (1.54184Å) |
| Absorption correction | analytical | gaussian | gaussian |
DFT calculations

The DFT calculations have been performed with the TURBOMOLE program package at the RI-[10]-B3LYP/[11]/def2-TZVP/[12] level of theory. The geometries were optimized in the gas phase using the Multipole Accelerated Resolution of Identity (MARI-J)/[13] approximation during the geometry optimization steps. The solvent effects were incorporated as single point calculations (without the RI approximation) on the gas phase optimized geometries via the Conductor-like Screening Model (COSMO)/[14] using the dielectric constant of CH₂Cl₂ (ε = 8.930). For the reaction energies the SCF energies, corrected for the “outlying charge” were used.

![Figure S2. Energy diagram of the reaction of 3 with pyridine at the B3LYP/def2-TZVP (ε = 8.930) level of theory. The positive charges, ligands added or cleaved are not depicted. [Mo] = CpMo(CO)₂.](image)

**Table S3.** Total Energies (a.u.) calculated at the B3LYP/def2-TZVP (ε = 8.930) level of theory.

|       | 1               | 3               | 4               | 5               | Py              |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Tot. Energy | -1659.5155691591 | -6931.7980095390 | -7428.2727777051 | -4605.715355024 | -248.2308381719 |
| Tot. Energy + OC corrections | -1659.5158776158 | -6931.792777731 | -7428.2672298176 | -4605.7059409177 | -248.2309357123 |

**Table S4.** Cartesian coordinates of the gas-phase optimized geometry of [[(Cp(CO)₂Mo)₂(μ-η²:η²-P₂)] (1) at the RI-B3LYP/def2-TZVP level of theory. (E = -1659.50357203601 a.u.).

| Atom | x               | y               | z               |      |
|------|-----------------|-----------------|-----------------|------|
| Mo   | -1.5559117      | 0.0069760       | 0.5627777       |      |
| Mo   | 1.5450011       | 0.0355811       | 0.5903500       |      |
| P    | -0.1014059      | -0.9509053      | 2.3433128       |      |
| P    | 0.0584393       | 1.1212438       | 2.2682024       |      |
| O    | -3.5539242      | 0.9665254       | 2.7784009       |      |
| O    | 3.5006702       | -0.7570687      | 2.9074333       |      |
| O    | -1.3936560      | 2.9857481       | -0.3975426      |      |
| O    | 1.3989772       | -3.0060285      | -0.1504782      |      |
| C    | -1.4078539      | 1.9016248       | -0.0066421      |      |
| C    | -2.7806282      | 0.6360565       | 1.9977310       |      |
| C    | 1.4064083       | -1.8960040      | 0.1595571       |      |
Table S5. Cartesian coordinates of the gas-phase optimized geometry of \([\text{Cp(CO)}_2\text{Mo}_2(\mu-\text{P}_2)]_2\text{Ag}_2]^2+\) (3) at the RI-B3LYP/def2-TZVP level of theory. (E = -6931.65150897001 a.u.).

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Ag   | 0.2667583 | 2.3084358 | 0.9091437 |
| Ag   | -0.2661552 | -2.3077761 | -0.9113967 |
| Mo   | 2.8016500 | -1.4843509 | 2.5534113 |
| Mo   | -0.0023169 | -1.4159941 | 3.9231411 |
| Mo   | 0.0021376 | 1.4167346 | -3.9240237 |
| Mo   | -2.8019964 | 1.4841757 | -2.5555183 |
| Mo   | -0.1721732 | 5.5453487 | 3.9710873 |
| Mo   | 0.4179510 | 6.7492946 | 1.1557833 |
| Mo   | 0.1706909 | -5.5466110 | -3.9711883 |
| Mo   | -0.4175390 | -6.7485643 | -1.1545810 |
| P    | 0.4620435 | -1.7815307 | 1.5175874 |
| P    | 0.9864416 | 0.1476421 | 2.1369227 |
| P    | -0.9863814 | -0.1476618 | -2.1384335 |
| P    | -0.4626543 | 1.7815802 | -1.5185236 |
| P    | 1.1794019 | 4.5145835 | 2.1675551 |
| Element | x-coordinate | y-coordinate | z-coordinate |
|---------|--------------|--------------|--------------|
| C       | 2.2591536    | 7.1043514    | 1.8593627    |
| C       | 2.0077505    | -6.3015878   | -3.7199671   |
| C       | 1.0503658    | -3.8153510   | -4.4005075   |
| C       | -2.2585492   | -7.1060766   | -1.8572177   |
| C       | -1.2545662   | -5.8514004   | 0.4005179    |
| C       | 3.7382518    | -0.9115568   | 4.7087983    |
| H       | 3.1880961    | -0.8917432   | 5.6334018    |
| C       | 3.9477211    | 0.1921507    | 3.8381629    |
| H       | 3.5675391    | 1.1899671    | 3.9797547    |
| C       | 4.7819893    | -0.2367422   | 2.7769092    |
| H       | 5.1557701    | 0.3811650    | 1.9765943    |
| C       | 5.0884496    | -1.6158947   | 2.9827701    |
| H       | 5.7469857    | -2.2187767   | 2.3793046    |
| C       | 4.4339891    | -2.0260430   | 4.1783038    |
| H       | 4.5012721    | -3.0034820   | 4.6285032    |
| C       | -0.4268998   | -3.7670855   | 4.1725650    |
| H       | -0.3845461   | -4.4633147   | 3.3525477    |
| C       | 0.6324069    | -3.4485182   | 5.0643696    |
| H       | 1.6197117    | -3.8766824   | 5.0524914    |
| C       | 0.1431688    | -2.5143532   | 6.0111059    |
| H       | 0.6949510    | -2.1073501   | 6.8432652    |
| C       | -1.2260104   | -2.2573028   | 5.7175204    |
| H       | -1.8935697   | -1.6360540   | 6.2917848    |
| C       | -1.5732355   | -3.0388982   | 4.5742149    |
| H       | -2.5488306   | -3.0993955   | 4.1197873    |
| C       | -4.4347204   | 2.0265492    | -4.1789071   |
| H       | -4.5026786   | 3.0044299    | -4.6280490   |
| C       | -3.7382024   | 0.9131307    | -4.7106033   |
| H       | -3.1881483   | 0.8946722    | -5.6352983   |
| C       | -3.9469030   | -0.1916521   | -3.8411172   |
| H       | -3.5660872   | -1.1890764   | -3.9837722   |
| C       | -4.7814954   | 0.2355272    | -2.7794323   |
| H       | -5.1548304   | -0.3835002   | -1.9797633   |
| C       | -5.0888939   | 1.6146781    | -2.9838258   |
| H       | -5.7478653   | 2.2164689    | -2.3797319   |
| C       | 1.9009737    | 5.9539331    | 5.1169920    |
| H       | 2.8635475    | 5.6815595    | 4.7172991    |
| C       | 1.2683737    | 7.2178741    | 4.9694926    |
| H       | 1.6710509    | 8.0693411    | 4.4484537    |
| C       | 0.0420777    | 7.1799111    | 5.6772075    |
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| H    | -0.6535980   | 7.9969547    | 5.7828763    |
| C    | -0.0879874   | 5.8962440    | 6.2745986    |
| H    | -0.8858214   | 5.5775484    | 6.9251936    |
| C    | 1.0708422    | 5.1373093    | 5.9238119    |
| H    | 1.2922839    | 4.1343061    | 6.2506375    |
| C    | -1.6758752   | 7.8452462    | 0.7185182    |
| H    | -2.6319316   | 7.3629100    | 0.8350645    |
| C    | -0.8881713   | 7.8569315    | -0.4579699   |
| H    | -1.147182    | 7.3896466    | -1.3939808   |
| C    | 0.2772459    | 8.6435809    | -0.2020400   |
| H    | 1.0497024    | 8.8902152    | -0.9119016   |
| C    | 0.1920167    | 9.1137650    | 1.1364915    |
| H    | 0.9031474    | 9.7628569    | 1.6220664    |
| C    | -1.0119857   | 8.6273767    | 1.7023991    |
| H    | -1.3814386   | 8.8512618    | 2.6882681    |
| C    | -1.0720508   | -5.1419064   | -5.9248751   |
| H    | -1.2937708   | -4.1394925   | -6.2533163   |
| C    | -1.9021410   | -5.9579454   | -5.1170627   |
| H    | -2.8649518   | -5.6849790   | -4.7181043   |
| C    | -1.2690865   | -7.2210706   | -4.9674717   |
| H    | -1.6716168   | -8.0718971   | -4.4452832   |
| C    | -0.0426102   | -7.1837417   | -5.6748768   |
| H    | 0.6533651    | -8.0007109   | -5.7791310   |
| C    | 0.0871697    | -5.9009453   | -6.2741847   |
| H    | 0.8850608    | -5.5829388   | -6.9250461   |
| C    | 1.6774336    | -7.8417926   | -0.7157083   |
| H    | 2.6329543    | -7.3582751   | -0.8317765   |
| C    | 0.8889364    | -7.8541227   | 0.4602498    |
| H    | 1.1467444    | -7.3862425   | 1.3962933    |
| C    | -0.2753307   | -8.6422858   | 0.2037696    |
| H    | -1.0479461   | -8.8896968   | 0.9131886    |
| C    | -0.1886292   | -9.1126873   | -1.1346057   |
| H    | -0.8966094   | -9.7628135   | -1.6204784   |
| C    | 1.0151673    | -8.6253651   | -1.6998054   |
| H    | 1.3855937    | -8.8487466   | -2.6853328   |
**Table S6.** Cartesian coordinates of the gas-phase optimized geometry of [(Cp(CO))₂Mo(P₂)₅Ag₂Py₂]²⁺ (4) at the RI-B3LYP/def2-TZVP level of theory. \( E = -7428.13056724068 \) a.u.

| Atom | \( x \) | \( y \) | \( z \) |
|------|-------|-------|-------|
| Ag | 2.5015903 | -0.7017092 | 0.4287429 |
| Mo | -0.2918152 | 1.8265599 | 3.7404305 |
| Mo | -0.8582052 | -1.2354844 | 3.8236871 |
| Mo | 6.9800910 | 0.4678159 | -0.7550506 |
| Mo | 6.4220825 | 1.5586320 | 2.1131258 |
| P | 0.6728574 | -0.0679811 | 2.2650877 |
| P | -1.3192515 | 0.4652308 | 1.9362832 |
| P | 4.8797813 | 0.2502311 | 0.7058859 |
| P | 6.5372318 | -0.8932819 | 1.2846577 |
| Ag | -2.5015626 | 0.7017687 | -0.4289885 |
| Mo | 0.2917884 | -1.8266228 | -3.7405169 |
| Mo | 0.8583002 | 1.2355072 | -3.8239159 |
| Mo | -6.9799431 | -0.4675679 | 0.7551702 |
| Mo | -6.4220727 | -1.5589206 | -2.1129333 |
| P | -0.6728409 | 0.0681059 | -2.2653584 |
| P | 1.3192233 | -0.4651996 | -1.9364525 |
| P | -4.8796952 | -0.2503577 | -0.7058427 |
| P | -6.5370750 | 0.8931177 | -1.2848614 |
| O | -1.7745270 | -3.1782851 | 1.5420900 |
| O | -3.8870216 | -0.5368029 | 4.3048969 |
| O | 1.3351600 | 3.5256789 | 1.6752112 |
| O | 2.4603568 | 1.2205882 | 5.1302644 |
| N | 2.6326986 | -3.1324780 | 0.7735435 |
| C | 1.5844862 | -3.9335133 | 0.5414674 |
| O | 9.3330969 | 0.6272430 | 2.8560852 |
| C | 2.8161402 | -5.8874904 | 1.1574520 |
| O | 5.0986280 | 2.7223577 | -1.8729506 |
| C | 3.9058655 | -5.0629035 | 1.4018616 |
| O | 5.3726746 | -1.6615560 | -2.3925037 |
| C | 1.6308570 | -5.3091400 | 0.7191681 |
| C | 3.7708710 | -3.6960351 | 1.1974199 |
| C | -2.0023923 | 2.1110059 | 5.4308986 |
| C | -2.4847177 | 2.6895130 | 4.2252984 |
| C | 1.0824364 | -2.0068025 | 5.0143920 |
| C | -0.5982516 | 3.8444734 | 4.8695940 |
| C | 9.2442350 | 1.3000452 | -0.5271983 |
| C | -0.8382442 | 2.8165175 | 5.8231286 |
C -0.9252144 -3.1215862  5.1922398
C  0.3463080 -3.1210968  4.5418478
C -2.7814249 -0.7493183  4.0918165
C -1.6241101  3.7601192  3.8798289
C  0.2776787 -1.3178064  5.9618721
C  9.3042524 -0.1205216 -0.5205991
C -1.4502745 -2.4291691  2.3457147
C  6.4347777  3.7969474  1.1930736
C  5.9273821 -0.8697693 -1.7715117
C  8.8283839 -0.5841919 -1.7704253
C  8.7210414  1.7118849 -1.7776332
C  5.7542801  1.8914455 -1.4257158
C -0.9596324 -1.9990918  6.0653312
C  8.4628561  0.5506230 -2.5568452
C  0.7454321  2.8588643  2.4000925
C  5.8007801  0.5213019  3.6985769
C  5.1100184  3.5256558  1.6563723
O  5.4372891 -0.0223980  4.6384660
C  8.2676755  0.9263037  2.5580320
C  1.4575527  1.3891920  4.5989613
C  7.3125335  3.7431372  2.3083323
C  5.1835658  3.3144859  3.0565999
C  6.5442133  3.4504669  3.4659021
O  1.7748644  3.1782701 -1.5423902
O  3.8871648  0.5368341 -4.3049109
O -1.3354430 -3.5255307 -1.6753285
O -2.4604710 -1.2207811 -5.1302412
O -9.3330189 -0.6274650 -2.8560609
O -5.0983063 -2.7217937  1.8734359
O -5.3724394  1.6621611  2.3920680
C  2.0023150 -2.1112527 -5.4310565
C  2.4846608 -2.6896114 -4.2253950
C -1.0824173  2.0068448 -5.0146366
C  0.5981578 -3.8446336 -4.8694908
C -9.2441733 -1.2997297  0.5276314
C  0.8381438 -2.8167851 -5.8231577
C  0.9252564  3.1215707 -5.1925366
C -0.3462524  3.121276 -4.5421284
C  2.7815353  0.7492975 -4.0919583
C  1.6240568 -3.7601798 -3.8797713
H  9.5829652  1.9500099  0.2608763
H  9.6836488  -0.733015  0.2799908
H  8.5836002  2.7310735 -2.1015195
H  8.1140631  0.5336810 -3.5761820
H  8.7892445 -1.6134711 -2.0884529
H  2.4665474 -1.3083386 -5.9769214
H  3.3713675 -2.3918946 -3.6907514
H  0.2598684 -2.6382015 -6.7155535
H -0.1774540 -4.5909374 -4.9224723
H  1.7484669 -4.4232177 -3.0392405
H -0.7005950  3.8632857 -3.8456297
H  1.6947117  3.8688929 -5.0887744
H  1.7711685  1.7400934 -6.7266087
H -0.5735077  0.4558488 -6.5346705
H -2.0912621  1.7492326 -4.7382014
H -0.2599892  2.6378390  6.7155182
H  0.1773609  4.5907691  4.9226687
H -1.7484918  4.4232457  3.0393654
H -3.3713863  2.3918368  3.6905713
H -2.4665669  1.3080384  5.9766526
H -1.7711986 -1.7401484  6.7263171
H -1.6946344 -3.8689401  5.0884491
H  0.5734748 -0.4558715  6.5344423
H  2.0913032 -1.7493918  4.7380363
H  0.7007263 -3.8632832  3.8454182
H -4.2250508 -3.5163446 -1.0547474
H -4.3476761 -3.1205896 -3.7077198
H -6.9148320 -3.3995125 -4.4760758
H -8.3730412 -3.9375130 -2.2828061
H -6.7101026 -4.0380836 -0.1804183
H -8.5835353 -2.7304975  2.1022075
H -9.5830070 -1.9498593 -0.2602645
H -9.6835424  0.7335307 -0.2798648
H -8.7889438  1.6140327  2.0883704
H -8.1137692 -0.5329073  3.5764013
**Table S7.** Cartesian coordinates of the gas-phase optimized geometry of \( [(\text{Cp}(\text{CO})_2\text{Mo})(\text{P}_2)_{\text{Ag}}\text{Py})_4]^{2+} \) (5) at the RI-B3LYP/def2-TZVP level of theory. \((E = -4605.6683848615\text{ a.u.})\).

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| Ag   | -0.3591501 | 0.1886761 | 2.4482339 |
| Mo   | 1.4617154 | -3.8616135 | 0.4530175 |
| Mo   | -1.6331555 | -3.8217096 | 0.1188955 |
| P    | -0.2444460 | -2.0660074 | 1.1797202 |
| P    | 0.1450430 | -2.2306300 | -0.8674992 |
| O    | -3.5680666 | -1.5988277 | -0.9551411 |
| O    | 1.0329233 | -4.3543539 | 3.5280625 |
| N    | 1.0169361 | 0.3004847 | 4.4040607 |
| O    | 3.4873539 | -1.5836817 | 1.1922645 |
| O    | -1.2404335 | -4.7900344 | -2.8463945 |
| C    | 2.1989406 | -0.7946572 | 6.1785240 |
| H    | 2.4698921 | -1.7237591 | 6.6613622 |
| C    | 2.2603375 | 1.5860938 | 5.9997950 |
| H    | 2.5803413 | 2.5617344 | 6.3396871 |
| C    | 2.6434194 | 0.4281977 | 6.6639578 |
| C    | 1.3916333 | -0.8125089 | 5.0508174 |
| H    | 1.0300985 | -1.7512090 | 4.6506859 |
| C    | 1.4506847 | 1.4767951 | 4.8799426 |
| H    | 1.1359398 | 2.3625593 | 4.3418742 |
| C    | 2.0796279 | -4.9721681 | -1.5890504 |
| H    | 1.7604311 | -4.6441300 | -2.5640918 |
| C    | -2.8207508 | -2.3826368 | -0.5857713 |
| C    | 2.7084683 | -2.3830188 | 0.9398944 |
| C    | -1.3510736 | -4.4156264 | -1.7664969 |
| C    | -3.5503289 | -5.1062553 | 0.4518915 |
| H    | -4.3531110 | -5.1280600 | -0.2666766 |
| C    | 1.1576273 | -4.1521587 | 2.4045242 |
| C    | 1.4260109 | -5.9420078 | -0.7813080 |
| H    | 0.5363746 | -6.4872255 | -1.0449996 |
| C    | 2.1877407 | -6.1141723 | 0.4007262 |
| H    | 1.9747001 | -6.8097635 | 1.1966295 |
| C    | -2.2852305 | -4.5843038 | 2.3042818 |
| H    | -1.9477171 | -4.1265428 | 3.2190599 |
| C    | -3.4411944 | -4.2247793 | 1.5697167 |
| H    | -4.1425264 | -3.4501654 | 1.8341295 |
| C    | 3.3234865 | -5.2598875 | 0.3278207 |
| H    | 4.1254663 | -5.2063610 | 1.0456629 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 3.2502121  | -4.5538420 | -0.9108866 |
| H       | 3.9825025  | -3.8571495 | -1.2850518 |
| C       | -2.4515295 | -6.0085787 | 0.5101862  |
| H       | -2.2717535 | -6.8247755 | -0.1711700 |
| C       | -1.6768595 | -5.6916344 | 1.6531277  |
| H       | -0.8091973 | -6.2274297 | 1.9971153  |
| N       | 2.5587628  | -0.3142661 | -3.4892186 |
| C       | 5.0558388  | -0.4572159 | -4.7172575 |
| C       | 4.9496266  | -0.3509804 | -3.3357095 |
| H       | 5.8285813  | -0.3212856 | -2.7055396 |
| C       | 2.6689842  | -0.4168052 | -4.8195718 |
| H       | 1.7415993  | -0.4402386 | -5.3785649 |
| C       | 3.8914879  | -0.4907142 | -5.4729742 |
| H       | 3.9233512  | -0.5726274 | -6.5510443 |
| C       | 3.6861536  | -0.2825116 | -2.7659514 |
| H       | 3.5705311  | -0.1992536 | -1.6919076 |
| Ag      | 0.3589837  | -0.1887466 | -2.4483257 |
| Mo      | -1.4617866 | 3.8616214  | -0.4530847 |
| Mo      | 1.6330575  | 3.8216470  | -0.1189306 |
| P       | 0.2443175  | 2.0659410  | -1.1797287 |
| P       | -0.1451678 | 2.2306183  | 0.8648782  |
| O       | 3.5679057  | 1.5987743  | 0.9552330  |
| O       | -1.0332026 | 4.3541307  | -3.5281984 |
| N       | -1.0169707 | -0.3005114 | -4.4042563 |
| O       | -3.4875148 | 1.5837126  | -1.1921549 |
| O       | 1.2404011  | 4.7900797  | 2.8463328  |
| C       | -2.1987744 | 0.7946915  | -6.1788156 |
| H       | -2.4696595 | 1.7238085  | -6.6616606 |
| C       | -2.2602644 | -1.5860618 | -6.0001269 |
| H       | -2.5802740 | -2.5616868 | -6.3400573 |
| C       | -2.6432449 | -0.4281419 | -6.6643136 |
| C       | -1.3915812 | 0.8125045  | -5.0510245 |
| H       | -1.0300691 | 1.7511886  | -4.6508320 |
| C       | -1.4507236 | -1.4768049 | -4.8791854 |
| H       | -1.1360668 | -2.3625852 | -4.3420938 |
| C       | -2.0796111 | 4.9723382  | 1.5889406  |
| H       | -1.7603696 | 4.6443612  | 2.5639857  |
| C       | 2.8206157  | 2.3825854  | 0.5858103  |
| C       | -2.7085953 | 2.3830376  | -0.9398376 |
| C       | 1.3510020  | 4.4156406  | 1.7664423  |
C  3.5502831  5.1061061  -0.4519534
H  4.3530547  5.1279062  0.2666249
C  -1.1577988  4.1520326  -2.4046306
C  -1.4260366  5.9421266  0.7811100
H  -0.5363909  6.4873623  1.0447289
C  -2.1878025  6.1142040  -0.4009075
H  -1.9747856  6.8097355  -1.1968682
C  2.2851946  4.5841410  -2.3043452
H  1.9476731  4.1263582  -3.2191074
C  3.4411306  4.2245914  -1.5697480
H  4.1424313  3.4499367  -1.8341214
C  -3.3235387  5.2599158  -0.3279074
H  -4.1255494  5.5339540  0.9108486
H  -3.9824966  3.8572948  1.2850936
C  2.4515245  6.0084718  -0.5103015
H  2.2717637  6.8246952  0.1710238
C  1.6768639  5.6915207  -1.6532453
H  0.8092298  6.2273388  -1.9972645
N  -2.5587705  0.3141690  3.4894387
C  -5.0556080  0.4573712  4.7179394
C  -4.9496593  0.3511296  3.3363734
H  -5.8287318  0.3214939  2.7063640
C  -2.6687376  0.4167930  4.8198140
H  -1.7412500  0.4401555  5.3786393
C  -3.8911149  0.4907723  5.4734426
H  -3.9227713  0.5726644  6.5515203
C  -3.6862957  0.2825830  2.7663818
H  -3.5708808  0.1992867  1.6923175
H  3.2746761  0.4778235  7.5417954
H  6.0258498  -0.5127037  -5.1944533
H  -6.0255254  0.5129357  5.1953156
H  -3.2744201  -0.4777331  -7.5422120
References

[1] (a) O. J. Scherer, J. Schwalb, H. Sitzmann, *Inorg. Synth.* 1990, 27, 224; (b) O. J. Scherer, H. Sitzmann, G. J. Wolmershäuser, *J. Organomet. Chem.* 1984, 268, C9.

[2] CrysAlisPro Software system, Rigaku Oxford Diffraction, (2015).

[3] R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* 1995, 51, 887-897.

[4] Sheldrick, G. M. *Acta Cryst.* 2015, A71, 3-8.

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

[6] Sheldrick, G. M. *Acta Cryst.* 2015, C27, 3-8.

[7] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth & Des.* 2014, 14, 3576–3586.

[8] O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Accts. Chem. Res.* 2008, 41, 1782-1789.

[9] a) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* 2014, 4, 91-100; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* 1989, 162, 165-169; c) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* 1995, 102, 346-354; d) TURBOMOLE V6.4, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, [http://www.turbomole.com](http://www.turbomole.com).

[10] a) K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 1995, 242, 652-660; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* 1997, 97, 119-124.

[11] a) P. A. M. Dirac, *Proc. Royal Soc. A* 1929, 123, 714-733; b) J. C. Slater, *Phys. Rev.* 1951, 81, 385-390; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 1980, 58, 1200-1211; d) A. D. Becke, *Phys. Rev. A* 1988, 38, 3098-3100; e) A. D. Becke, *J. Chem. Phys.* 1993, 98, 5648-5652; f) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, 37, 785-789.

[12] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Letters* 1998, 294, 143-152; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, 7, 3297-3305.

[13] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* 2003, 118, 9136-9148.

[14] a) A. Klamt; G. Schüürmann. *J. Chem. Soc. Perkin Trans.2, 1993*, 5, 799–805; b) A. Klamt; V. Jonas, *J. Chem. Phys., 1996*, 5, 9972–9981.