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Supporting Information for:

1,2,3-triphospholyl derivatives as reactive intermediates

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S1. Experimental Section and analytical characterisation

General remarks:

All manipulations were performed under an atmosphere of dry nitrogen using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. The starting materials **1** and **2** were prepared according to published methods. [1] Solution NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. Mass spectra were performed using a Finnigan MAT 95 (FD-MS and EI-MS).

Synthesis of 3: A solution of 1,2-diphosphinobenzene (62 mg, 0.44 mmol) was added to a solution of [Cp*P{W(CO)$_5$}$_2$] (**1**) (175 mg, 0.22 mmol) in toluene (20 ml) at room temperature. The blue colour of **1** turns to orange after 16 hours stirring at room temperature. The reaction mixture was concentrated to circa 2 ml and layered with 5 ml hexane. **3**·1.5CH$_2$Cl$_2$ (27 mg, 8%) crystallises as pale yellow crystals. MS (EI, 70 eV) *m/z* 1636 (M$^+$, 2%), 1312 (M$^+$-W(CO)$_5$, 2). IR (KBr) ν_{max}/cm^{-1} 2068m, 1998vs, 1946s (CO).

Synthesis of 4: A solution of 1,2-diphosphinobenzene (58 mg, 0.41 mmol) was added to a solution of [Cp*As{W(CO)$_5$}$_2$] (**2**) (172 mg, 0.20 mmol) in toluene (20 ml) at -78 °C. After the reaction mixture was allowed to slowly warm up to room temperature and stirred for two days, the colour of the reaction mixture turns to brown. The reaction mixture was concentrated to circa 5 ml and layered with 5 ml hexane. **4**·C$_6$H$_5$CH$_3$ (38 mg, 11%) crystallises as pale yellow crystals. ^{1}H NMR δ_H (400 MHz; CD$_2$Cl$_2$; Me$_4$Si) 4.77 (1 H, m, As–*H*), 6.94 (1 H, dm, J_{HP} 321, P–*H*), 8.10 (8 H, m, C$_6$*H*$_4$). ^{31}P{^{1}H} NMR δ_P (161 MHz; CD$_2$Cl$_2$; Me$_4$Si) -31.5 (1 P, ddd, J_{PP} 4, J_{PP} 13, J_{PP} 17, P^4), 13.4 (1 P, ddd, J_{PP} 3, J_{PP} 12, J_{PP} 13, P^1), 41.1 (1 P, ddd, J_{PP} = 229, J_{PP} 4, J_{PP} 12, P^3), 61.3 (1 P, ddd, J_{PP} 229, J_{PP} 4, J_{PP} 17, P^2). IR (KBr) ν_{max}/cm^{-1} 2068s, 1998s, 1920vs (CO). MS (EI, 70 eV) *m/z* 1723 (M$^+$, 2%), 1695 (M$^+$- CO, 2), 862 (½·M$^+$, 42)

Trapping reactions with 2,3-dimethylbuta-1,3-diene

Synthesis of 5: A solution of 2,3-dimethylbuta-1,3-diene (83 mg, 1.00 mmol) was added to a solution of [Cp*P{W(CO)$_5$}$_2$] (**1**) (163 mg, 0.20 mmol) and 1,2-phenylendiphosphine (30mg, 0.20 mmol) in toluene (20 ml) at -78 °C. After the reaction mixture was allowed to slowly warm up to room temperature and stirred for two days, the colour of the reaction mixture turns to brown. From the concentrated reaction mixture **5** was identified by ^{31}P NMR spectroscopy. The yield of **5** is 20% estimated from the ^{31}P NMR of the reaction mixture.

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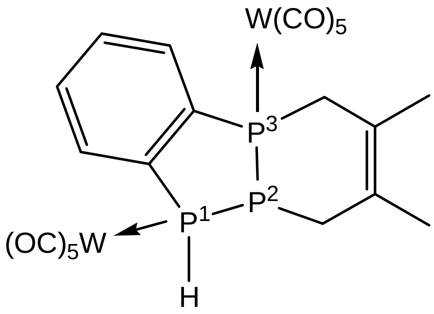
$^{31}P\{^1H\}$ NMR: δ_P (161 MHz; C_6D_6; Me_4Si) 28.9 (1 P, dd, J_{PP} 287, J_{PP} 19, J_{PW} 235, P^3), -30.0 (1 P, dd, J_{PP} 267, J_{PP} 19, J_{PW} 229, P^1), -66.2 (1 P, dd, J_{PP} 267, J_{PP} 287, J_{PW} 22, J_{PW} 25, P^2). ^{31}P NMR: δ_P (161 MHz; C_6D_6; Me_4Si) 28.9 (1 P, m, J_{PP} 287, J_{PP} 19, J_{PW} 235, P^3), -30.0 (1 P, m, J_{PH} 318, J_{PP} 267, J_{PP} 19, J_{PW} 229, P^1), -66.2 (1 P, m, J_{PP} 267, J_{PP} 287, J_{PW} 22, J_{PW} 25, P^2).



5

Numbering scheme in **5**.

Synthesis of 6: A solution of 2,3-dimethylbuta-1,3-diene (83 mg, 1.00 mmol) was added to a solution of [Cp*As{$W(CO)_5$}$_2$] (**2**) (172 mg, 0.20 mmol) and 1,2-phenylendiphosphine (30mg, 0.20 mmol) in toluene (20 ml) at -78 °C. After the reaction mixture was allowed to slowly warm up to room temperature and stirred for two days, the colour of the reaction mixture turns to yellow. The reaction mixture was concentrated to about 5 ml and layered with 6 ml hexane. **6** (37 mg, 19%) precipitates as a yellow crystalline solid. $^{31}P\{^1H\}$ NMR: δ_P (161 MHz; CD_2Cl_2; Me_4Si) -41.7 (1 P, d, J_{PP} 17, J_{PW} 229, P), 35.8 (1 P, d, J_{PP} 17, J_{PW} 225, *P*H). ^{31}P NMR: δ_P (161 MHz; CD_2Cl_2; Me_4Si) -41.7 (1 P, m, J_{PW} 229, P), 35.8 (1 P, dm, J_{PH} 323, J_{PW} 225, *P*H). MS (FD, CH_2Cl_2): *m/z* 944 (M^+, 100%).

Cp*H (CH_2Cl_2): δ[ppm]: 0.91(m, 3H), 1.66(m, 6H), 1.73(m,6H), 2.32 (m. 1H).

Experimental and simulated $^{31}P\{^1H\}$ NMR spectrum of 4.

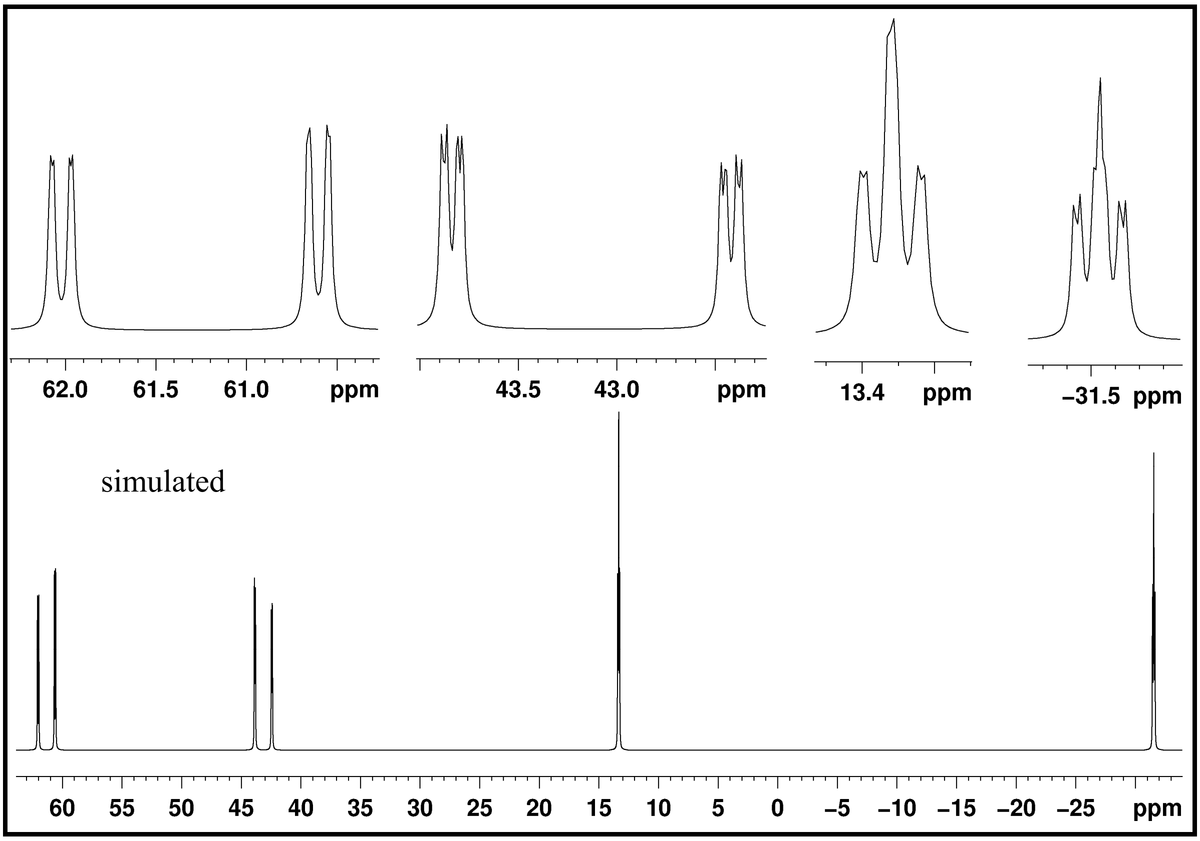


Fig. 1 Simulated $^{31}P\{^1H\}$ NMR spectrum of **4**.

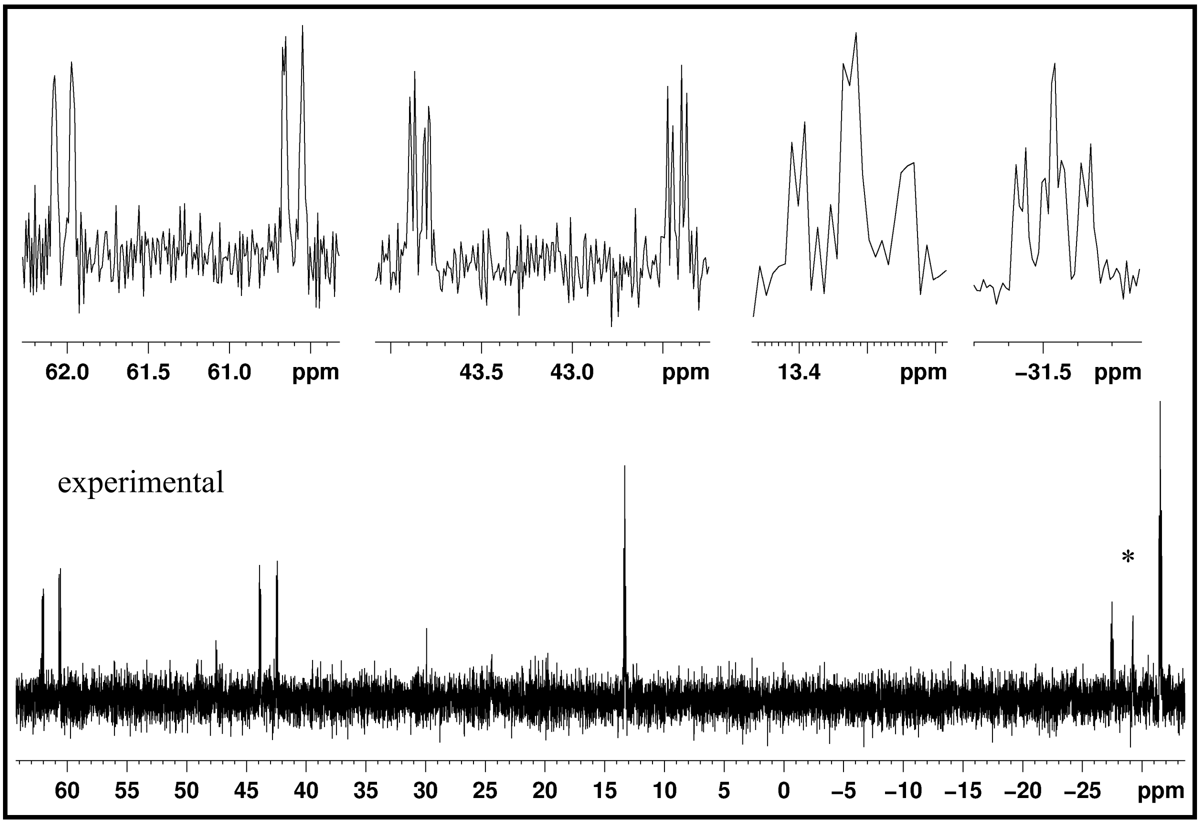


Fig. 2 Experimental $^{31}P\{H\}$ NMR spectrum of **4** at 300K in CD_2Cl_2 (∗ = impurity).

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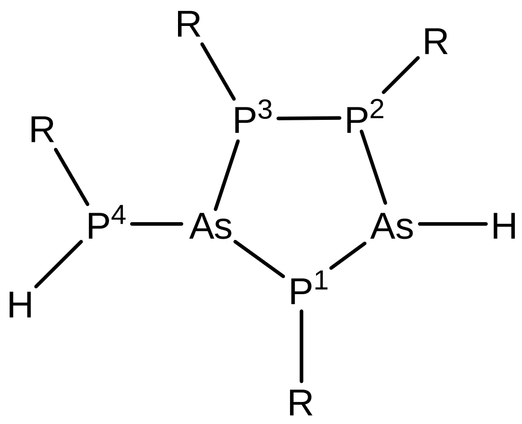


Numbering scheme of the ADMX spin system in **4**.

Coupling constants determined from the simulation of the ^{31}P NMR spectrum of **4.**

P^1–P^2	J_{PP} = 3.3 Hz [a)]
P^1–P^3	J_{PP} = 12.7 Hz [a)]
P^1–P^4	J_{PP} = 13.3 Hz [a)]
P^2–P^3	$^1J_{PP}$ = 229.7 Hz
P^2–P^4	$^3J_{PP}$ = 17.3 Hz
P^3–P^4	$^2J_{PP}$ = 4.4 Hz

[a)] The coupling is to be considered as a sum of a $^2J_{PP}$ and $^3J_{PP}$ coupling.

S2. Crystallographic details

Crystal structure analysis: By cooling a CH_2Cl_2/hexane solution of **3** at –25 °C yellow prisms suitable for X-ray crystallography were obtained. Compound **4** crystallise from a toluene solution at room temperature as a **4**·$C_6H_5CH_3$ solvate. The crystal structure analysis of **3** and **4** were performed on an Oxford Diffraction Gemini R Ultra diffractometer using $Cu_{K\alpha}$ radiation (λ = 1.54178Å). The structures were solved by direct methods with the programs SHELXS-97[2] for **4** and SIR-97[3] for **3**, and full matrix least squares refinement on F^2 in SHELXL-97 was performed with anisotropic displacements for non-H atoms. Hydrogen atoms at the carbon atoms were located in idealised positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus and arsenic atoms could be located by residue electron densities and refined in dependence of the corresponding heavy atom.

Crystal data for **3**·CH_2Cl_2: $C_{33}H_{12}O_{20}Cl_2P_6W_4$, M = 1720.51, triclinic, space group $P\bar{1}$, a = 11.547(3), b = 14.237(3), c = 17.070(7) Å, α = 111.295(6), β = 104.846(7), γ = 99.201(18)°, V = 2425.6(13) Å^3, T = 123.0(1) K, Z = 2, $\mu(Cu_{K\alpha})$ = 20.615 mm^{-1}, 10270 reflections measured, 6061 unique (Rint = 0.027) which were used in all calculations. The final R_1 [I > 2σ(I)] was

0.0301. The position of the hydrogen atoms bonded to phosphorus in **3**·CH_2Cl_2 was located on the Fourier map and isotropically refined. With the help of PLATON[4] a solvent accessible areas was found, but it was impossible to refine any reasonable molecule from difference Fourier peaks. Therefore the midpoint, the size and the number of electrons in these voids were refined and the contribution to the calculated structure factors of the disordered solvent is taken into account by back-Fourier transformation with the program SQUEEZE[5]. The void was found at (0.500, 1.000, 0.500) the sizes is 96 $Å^3$, 38 e^-. This electron number corresponds to one CH_2Cl_2 molecule. All crystals were intergrown small rods. A treatment of the data to enable the refinements with the shelxl hklf5 option was not possible, therefore only the uninfluenced reflections were used for structural calculations. This leads to low data completeness (79%). The fairly low resolution of the data set is due to the technical setup used at the time of measuring the structure of **3** which limited the highest possible resolution to 0.87Å.

Crystal data for **4**·$C_6H_5CH_3$: $C_{39}H_{18}As_2O_{20}P_4W_4$, M = 1815.61, triclinic, space group $P\bar{1}$, a = 12.2685(5), b = 12.4386(5), c = 18.7689(7) Å, α = 96.500(3), β = 102.035(4), γ = 115.791(4)°, V = 2453.6(2) $Å^3$, T = 123(1) K, Z = 2, $\mu(Cu_{K\alpha})$ = 20.288 mm^{-1}, 13743 reflections measured, 7523 unique (Rint = 0.0401) which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0390.

The cavity in the crystal structure of **4** is slightly larger than necessary for a toluene molecule which causes the slight spinning of the solvent molecule. This leads to the somewhat lager e.s.d.s.

Comparison of the molecular structure of 3 and 4.

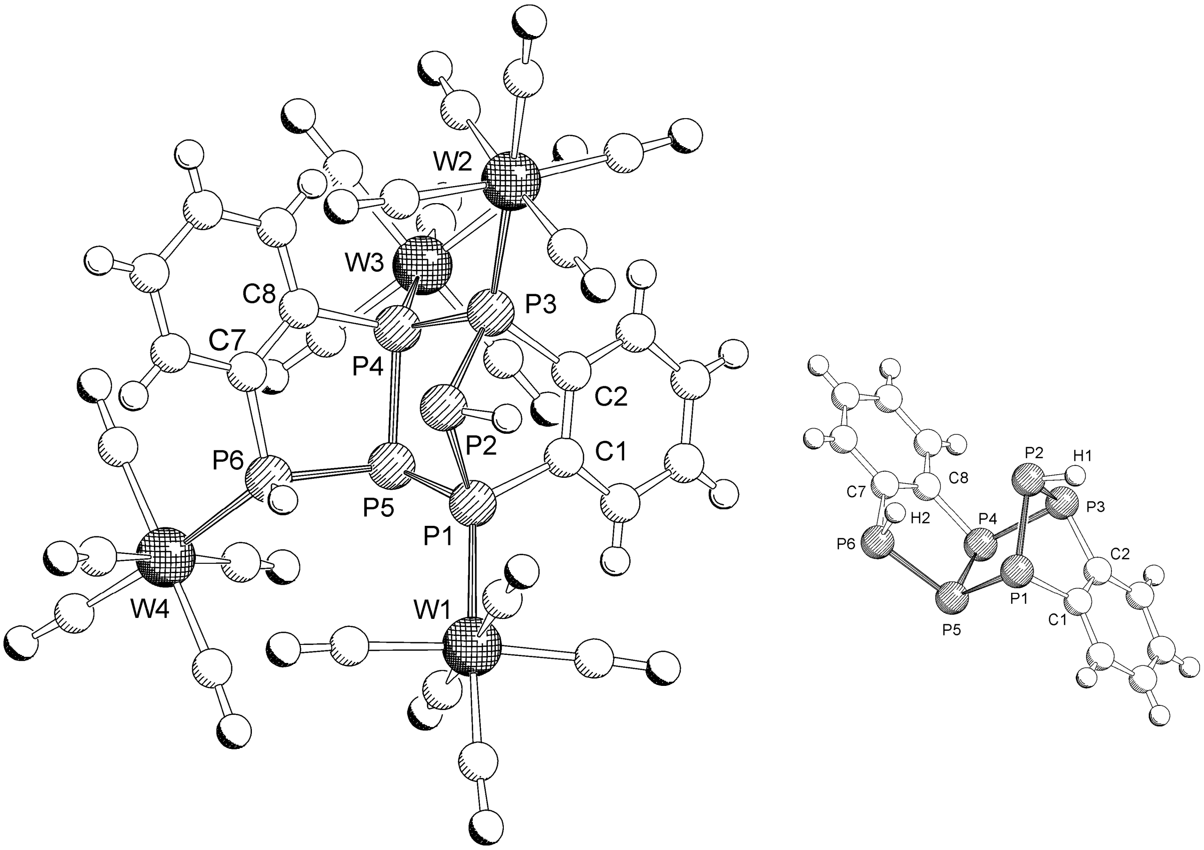
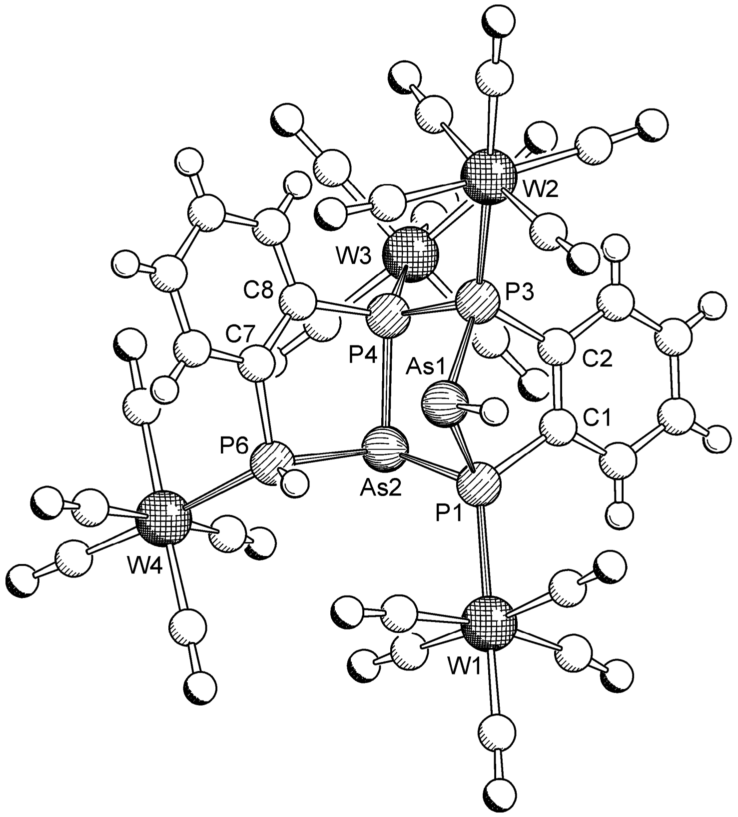


Fig. 3 Molecular structure of 1,3,6,7-tetrakis(pentacarbonyl-wolfram)-4,5,8,9-dibenzo-1,3,6,7-hexaphospha-exo-tricyclo-[5.2.1.0^{2,6}]-decan (**3**) (left). Central core in **3** (right). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.478(2), P(1)–P(2) 2.193(3), P(2)–P(3) 2.191(4), P(3)–C(2) 1.824(9), P(3)–P(4) 2.259(3), P(4)–C(8) 1.834(10), P(4)–P(5) 2.244(3), W(2)–P(3) 2.478(2), P(5)–P(6) 2.216(3), P(6)–C(7) 1.831(9), P(2)–H(1) 1.2300, P(6)–H(2) 1.2300, W(3)–P(4) 2.490(2), W(4)–P(6) 2.475(3), P(1)–P(5) 2.238(3), P(1)–C(1) 1.828(8); P(5)–P(6)–C(7) 100.3(3), P(3)–P(2)–H(1) 98.00, P(1)–P(2)–H(1) 94.00, W(4)–P(6)–H(2) 118.00, W(1)–P(1)–P(2) 116.41(11), C(7)–P(6)–H(2) 95.00, W(1)–P(1)–P(5) 120.79(11), P(5)–P(6)–H(2) 105.00, W(1)–P(1)–C(1) 122.0(3), P(1)–C(1)–C(6) 122.3(6), P(2)–P(1)–P(5) 100.51(12), P(2)–P(1)–C(1) 99.0(3), P(5)–P(1)–C(1) 93.2(3), P(1)–P(2)–P(3) 91.26(12), W(2)–P(3)–P(2) 111.40(11), W(2)–P(3)–P(4) 123.03(11), W(2)–P(3)–C(2) 125.2(3), P(2)–P(3)–P(4) 97.48(12), P(2)–P(3)–C(2) 98.9(3), P(4)–P(3)–C(2) 95.3(3), W(3)–P(4)–P(3) 119.67(11), W(3)–P(4)–P(5) 110.77(11), W(3)–P(4)–C(8) 118.0(3), P(3)–P(4)–P(5) 101.54(12), P(3)–P(4)–C(8) 103.8(3), P(5)–P(4)–C(8) 100.2(3), P(1)–P(5)–P(4) 101.12(12), P(1)–P(5)–P(6) 100.79(12), P(4)–P(5)–P(6) 95.88(12), W(4)–P(6)–P(5) 116.24(11), W(4)–P(6)–C(7) 118.5(3).



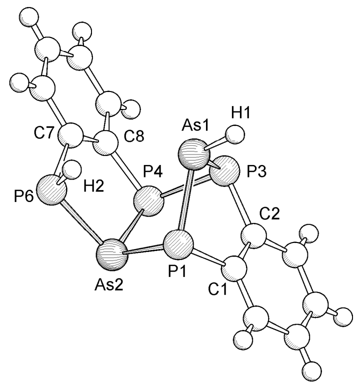


Fig. 4 Molecular structure of 1,3,6,7-tetrakis(pentacarbonyl-wolfram)-4,5,8,9-dibenzo-1,3,6,7-tetraphospha-2,10-diarsa-exo-tricyclo-[5.2.1.0^{2,6}]-decan (**4**) (left). Central core in **4** (right). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.479(2), P(1)–As(1) 2.315(2), As(1)–P(3) 2.312(3), P(3)–C(2) 1.816(9), P(3)–P(4) 2.266(3), P(4)–C(8) 1.830(10), P(4)–As(2) 2.337(2), W(2)–P(3) 2.5011(19), As(2)–P(6) 2.335(3), P(6)–C(7) 1.836(8), As(1)–H(1) 1.4600, P(6)–H(2) 1.21(10), W(3)–P(4) 2.498(3), W(4)–P(6) 2.479(2), P(1)–As(2) 2.347(2), P(1)–C(1) 1.837(10); As(2)–P(6)–C(7) 100.6(3), P(3)–As(1)–H(1) 114.00, P(1)–As(1)–H(1) 114.00, W(4)–P(6)–H(2) 127(5), W(1)–P(1)–As(1) 117.09(11), C(7)–P(6)–H(2) 94(4), W(1)–P(1)–As(2) 116.21(8), As(2)–P(6)–H(2) 104(5), W(1)–P(1)–C(1) 123.7(3), P(1)–C(1)–C(6) 121.6(6), As(1)–P(1)–As(2) 99.96(9), As(1)–P(1)–C(1) 98.5(3), As(2)–P(1)–C(1) 96.9(3), P(1)–As(1)–P(3) 87.57(9), W(2)–P(3)–As(1) 113.23(10), W(2)–P(3)–P(4) 120.23(10), W(2)–P(3)–C(2) 124.1(3), As(1)–P(3)–P(4) 100.00(10), As(1)–P(3)–C(2) 98.2(3), P(4)–P(3)–C(2) 96.4(3), W(3)–P(4)–P(3) 119.20(11), W(3)–P(4)–As(2) 107.51(9), W(3)–P(4)–C(8) 121.5(3), P(3)–P(4)–As(2) 102.96(10), P(3)–P(4)–C(8) 102.1(3), As(2)–P(4)–C(8) 100.7(3), P(1)–As(2)–P(4) 98.68(7), P(1)–As(2)–P(6) 101.00(9), P(4)–As(2)–P(6) 92.71(9), W(4)–P(6)–As(2) 113.60(10), W(4)–P(6)–C(7) 113.7(3).

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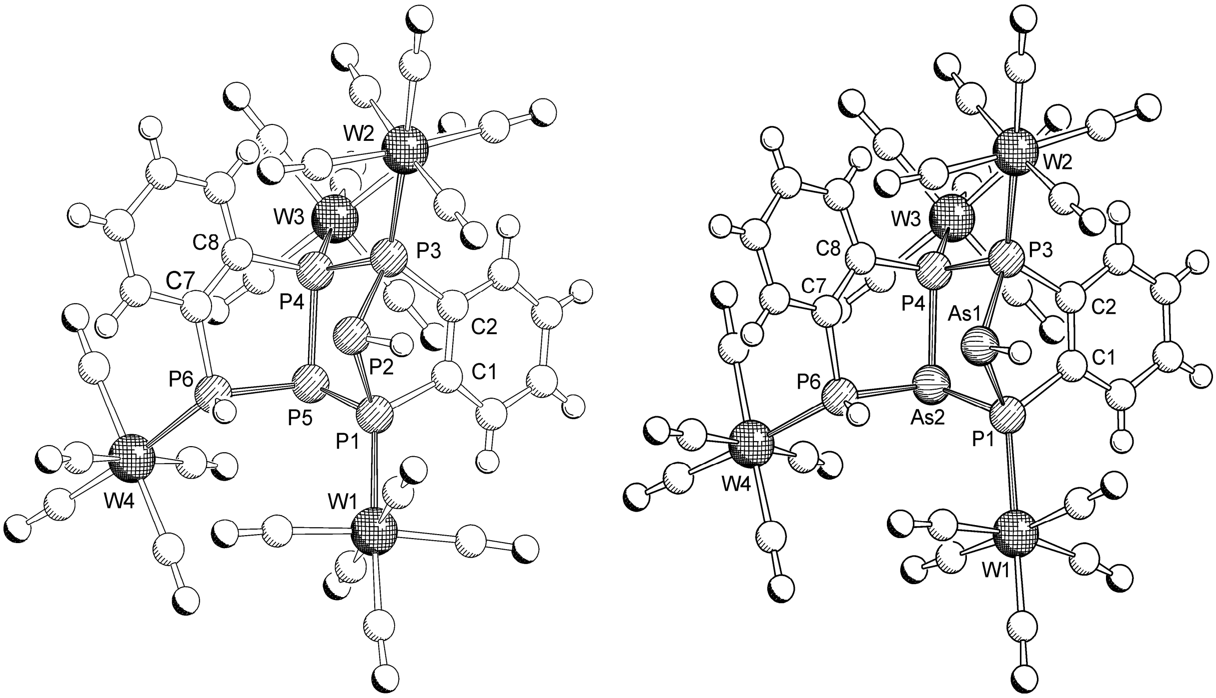

Fig. 5 Molecular structure of **3** (left) and **4** (right).

Table 1: Comparison of bond lengths [Å] and angles [°] in the crystal structures of **3** and **4**.

3		**4**	
P3–P4	2.259(3)	2.266(3)	P3–P4
P–C	1.824(9) – 1.834(10)	1.816(9) – 1.837(10)	P–C
P–W	2.475(3) – 2.490(2)	2.479(2) – 2.5011(19)	P–W
P5–P1–P2	100.51(12)	99.96(9)	As2–P1–As1
P1–P2–P3	91.26(12)	87.57(9)	P1–As1–P3
P2–P3–P4	97.48(12)	102.00(10)	As1–P3–P4
P3–P4–P5	101.54(12)	102.96(10)	P3–P4–As2
P4–P5–P1	101.12(12)	98.68(7)	P4–As2–P1
P4–P5–P6	95.88(12)	92.71(9)	P4–As2–P6
P6–P5–P1	100.79(12)	101.00(9)	P6–As2–P1

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