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General remarks

All experiments were performed under argon atmosphere using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried on a Schlenk line or kept at 120 °C overnight prior to use. Solvents were degassed prior to the filtration over alumina in the PureSolv purification system by “inert”, the water content was determined by Karl Fischer titration. Solvents were additionally tested using a ketyl test to guarantee oxygen and moisture free conditions and stored over 4 Å molecular sieves under Ar. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves under Ar. The argon was provided by PANGAS and further purified with an MBraun >99 HP gas purification system. Air sensitive compounds were handled in a glovebox (MBraun lab master 130 or 150B-G). Small scale reactions were performed inside a glovebox. Chemicals were received from ABCR, Acros, Aldrich, Fluka, Lancaster or STREM. $P_3C_3(OBR_2)_3^1$ was synthesized following literature procedures.

IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500 - 4000 cm^{-1}). For solid compounds the ATR technique was used. The absorption bands are described as follows: very strong (vs), strong (s), middle (m), weak (w), or broad (br).

NMR measurements were carried out on Bruker Avance 200, 250, 300, 400, 500 MHz and 500 MHz cryoprobe spectrometers at room temperature (unless indicated otherwise). Chemical shifts δ are given as dimensionless numbers and the absolute values of the coupling constants are given in Hertz (Hz), the first atom mentioned in the subscript always refers to the atom that was used to observe the coupling. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). NMR spectra were referenced to TMS (1H , ^{13}C), H_3PO_4 (^{31}P) and Na_2WO_4 (^{183}W).

X-ray single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a glovebox, selected under a microscope with polarized light and transferred to a Mitegen micro-mount. The measurements were performed while cooling the crystals to 100 K. For structure solution and refinement, the programs SHELXT and SHELXL embedded in the OLEX² program suite were used.¹⁻⁴ Details of the structure determinations are given in Tables 1-7 in the crystallographic part. All non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC 2234729-2234735 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

1. G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **64** (2008), pp. 112–122.
2. G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **71**, 3–8 (2015).
3. G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **71**, 3–8 (2015).
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–341 (2009).

Experimental procedures

General procedure for the preparation of $[M(P_3C_3(OB(ipc)_2)_3)(CO)_3]$ complexes (M = Cr, W): Cr P_3C_3 -B, W P_3C_3 -B.

P_3C_3 -B (100 mg, 0.1 mmol) in *n*-hexane (5 mL) was dropwise added to $[Cr(CO)_3(MeCN)_3]$ (31 mg, 0.1 mmol) in 5 mL THF. The reaction mixture turned dark red and was stirred overnight. The solvent and volatiles were removed *in vacuo* and the red product was dissolved in *n*-hexane and filtered. The volume of the solution mixture was reduced before it was placed in a $-18\text{ }^\circ\text{C}$ freezer. Red crystals were isolated by filtration and washed with *n*-hexane (0.5 mL). The filtrate still showed a high concentration of the product. Repeating the procedure increased the yield. By slow evaporation of the solvent red crystals suitable for X-ray diffraction were obtained.

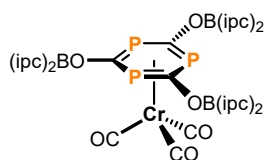
Cr P_3C_3 -B

$[Cr(P_3C_3(OB(ipc)_2)_3)(CO)_3]$

Yield: 81 mg (72%)

MF: $C_{66}H_{102}B_3O_6P_3Cr$

MW: 1168.9 g/mol



1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.41-2.37 (m, 1H, CH), 2.35 – 2.19 (m, 1H, CH), 2.07 – 1.84 (m, 2H, CH), 1.84 – 1.69 (m, 2H, CH), 1.18 (s, 3H, CH_3), 1.03 – 0.92 (m, 6H, CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) 232.3 (s, CO), 164.4 (s, $^1J_{CP} = 71.7$ Hz, PC ring), 48.1 (s), 41.3 (s), 39.0 (s), 37.6 (s), 33.9 (s), 28.7 (s), 23.7 (s), 23.0 (s).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ (ppm) 17.4 (s, 3P).

IR [cm^{-1}] powder: 2893, 2012 (CO), 1967 (CO), 1470, 1450, 1365, 1305, 1261, 1224, 1178, 1129, 1029.

E.A. [calc]: C 67.82; H 8.80; E.A.[found]: C 67.78; H 8.82.

Absorption max [λ nm]: 414, 478.

CCDC 2234732.

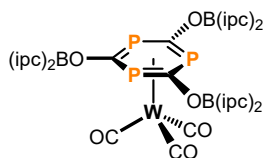
W P_3C_3 -B

$[W(P_3C_3(OB(ipc)_2)_3)(CO)_3]$

Yield: 71 mg (56%)

MF: $C_{66}H_{102}B_3O_6P_3W$

MW: 1300.7 g/mol



1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.36 – 2.29 (m, 2H, CH), 1.98 – 1.86 (m, 2H, CH), 1.87 – 1.78 (m, 1H, CH), 1.73 (m, 1H, CH), 1.19 (s, 3H, CH_3), 1.02 – 0.96 (m, 6H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ (ppm) 210.9 (s, CO), 149.0 (s, $^1J_{\text{CP}} = 80.1$ Hz, PC ring), 48.1 (s), 41.3 (s), 39.0 (s), 37.5 (s), 33.9 (s), 29.6 (s), 28.7 (s), 27.0 (s), 23.7 (s), 23.1 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ (ppm) -1.6 (s, 3P, $J_{\text{WP}} = 21.4$ Hz).

^{183}W NMR (203 MHz, C_6D_6): δ (ppm) -3146 ($J_{\text{WP}} = 19.9$ Hz).

IR [cm^{-1}] powder: 2902 (br), 2019 (s, CO), 1963 (s, CO), 1449, 1437, 1345, 1176, 1130, 1054.

E.A. [calc]: C 60.94; H 7.90; E.A.[found]: C 61.18; H 7.46

Absorption max [λ nm]: 392, 482.

CCDC 2234733.

General procedure for the preparation of $[\text{M}(\text{P}_3\text{C}_3(\text{OSi}^t\text{BuPh}_2)_3)\text{CO}]_3$ complexes (M = Cr, W): Cr $\text{P}_3\text{C}_3\text{-Si}$, W $\text{P}_3\text{C}_3\text{-Si}$.

$\text{P}_3\text{C}_3\text{-B}$ (300 mg, 0.3 mmol) was dissolved in 10 mL THF and a solution of $^t\text{BuOH}$ (0.8 mL, 8.7 mmol) in 5 mL THF was added dropwise to the solution. To the yellow clear solution $^t\text{BuSiPh}_2\text{Cl}$ (0.8 mL, 2.6 mmol) was added and a solution of DBU (0.1 mL, 0.9 mmol) in THF was added dropwise to the solution which turned darker upon addition. $[\text{Cr}(\text{MeCN})_3(\text{CO})_3]$ (112 mg, 0.4 mmol) was added and the reaction mixture was stirred overnight until full conversion was reached. The solution was dried under reduced pressure and the brown residue was extracted with *n*-hexane (3 x 10 mL). The orange solutions were combined and filtered through Celite. After reducing the volume of the solvent, the orange solution was placed in a -18°C freezer overnight. Orange crystals were collected by filtration and washed with 3 x 0.4 mL pentane. The product was dried *in vacuo* to yield an orange product. The filtrate and washings still showed a high concentration of the product. Therefore, the procedure was repeated to increase the yield of the reaction. By slow evaporation of the product in *n*-hexane orange crystals suitable for X-ray analysis were obtained.

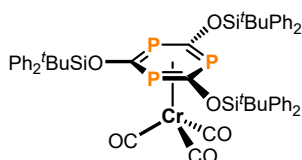
Cr $\text{P}_3\text{C}_3\text{-Si}$

$[\text{Cr}(\text{P}_3\text{C}_3(\text{OSi}^t\text{BuPh}_2)_3)\text{CO}]_3$

Yield: 33 mg (11%)

MF: $\text{C}_{54}\text{H}_{57}\text{Si}_3\text{O}_6\text{P}_3\text{Cr}$

MW: 1031.2 g/mol.



^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.49 (d, $^1J_{\text{HH}} = 7.3$ Hz, 4H, Ph), 7.38 (d, $^1J_{\text{HH}} = 7.3$ Hz, 2H, Ph), 7.26 (t, $^1J_{\text{HH}} = 7.5$ Hz, 4H, Ph), 1.08 (s, 9H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz): δ (ppm) 235.0 (s, CO), 168.9 (s, $^1J_{\text{CP}} = 73.1$ Hz, PC ring), 136.5 (s, Ph), 131.3 (s, Ph), 130.0 (s, Ph), 127.4 (s, Ph), 26.9 (s, ^tBu), 19.7 (s, ^tBu).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 203 MHz): δ (ppm) 22.5 Hz (s, 3P)

IR [cm^{-1}] powder: 2961, 2860, 1983 (CO), 1927 (CO), 1427, 1104, 1076, 695.

E.A. [calc]: C 62.90; H 5.57; E.A.[found]: C 62.79; H 5.88.

Absorption max [λ nm]: 421, 485.

CCDC 2234730.

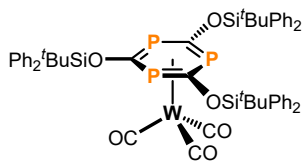
W P₃C₃-Si



Yield: 34 mg (10%)

MF: C₅₄H₅₇Si₃O₆P₃W

MW: 1163.0 g/mol.



¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.47 (d, ¹J_{HH} = 7.2 Hz, 4H, Ph), 7.38 (d, ¹J_{HH} = 7.4 Hz, 2H, Ph), 7.26 (q, ¹J_{HH} = 7.5 Hz, 4H, Ph), 1.05 (s, 9H, CH₃).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 213.7 (s, CO), 154.0 (s, ¹J_{CP} = 82.7 Hz, PC ring), 136.5 (s, Ph), 131.2 (s, Ph), 130.0 (s, Ph), 127.4 (s, Ph), 26.8 (s, ^tBu), 19.6 (s, ^tBu).

³¹P{¹H} NMR (203 MHz, CDCl₃): δ (ppm) 6.5 (s, 3P, J_{W,P} = 19.1 Hz).

¹⁸³W NMR (203 MHz, THF-d₈): δ (ppm) -3140 (J_{W,P} = 20.2 Hz).

IR [cm⁻¹] powder: 3056, 1989 (CO), 1921 (CO), 1428, 1103, 1058, 690, 508.

E.A. [calc]: C 55.77; H 4.94; E.A.[found]: C 55.53; H 5.02.

Absorption max [λ nm]: 392, 479.

CCDC 2234735.

General procedure for the preparation of [M(P₃C₃(OH)₃)(CO)₃] complexes (M = Cr, Mo, W): Cr P₃C₃-H, Mo P₃C₃-H and W P₃C₃-H.

Cr P₃C₃-B (25 mg, 0.02 mmol) was dissolved in 2 mL *n*-hexane. To the solution, 2 mL dry MeOH was added. The reaction mixture was shaken and after the separation of the phases, the methanol phase that contains the product was isolated. The solvent was removed and the product was washed with *n*-hexane before drying *in vacuo*. Single crystals suitable for X-ray diffraction studies were obtained from a *n*-hexane solution of Cr P₃C₃-B in the presence of ^tBuOH at -18 °C.

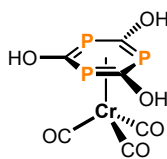
Cr P₃C₃-H



Yield: 6 mg (55%)

MF: C₁₂H₂₇CrO₁₂P₃

MW: 508.3 g/mol



³¹P{¹H} NMR (203 MHz CDCl₃): δ (ppm) -7.4 (s, 3P).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 235.6 (s, CO), 171.9 (s, ¹J_{CP} = 69.7 Hz, PC ring).

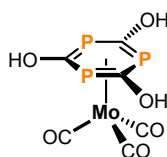
No resonance signal for the OH groups attached to the P₃C₃ is observed in the ¹H NMR spectrum, indicating that rapid exchange occurs on the NMR time scale.

IR (cm⁻¹): 2974, 2868, 1980 (CO), 1921 (CO), 1453, 1366, 1312, 1069, 1033, 909.

E.A. [calc] for C₃₀H₆₃O₁₂P₃Cr (Cr P₃C₃-H + 6 ^tBuOH): C 47.37; H 8.35; E.A.[found]: C 47.81; H 8.60.

CCDC 2234731.

Mo P₃C₃-H



[MoP₃C₃(OH)₃](CO)₃·x[tBuOH]₆

Yield: 7 mg (61%)

MF: C₁₂H₂₇MoO₁₂P₃

MW: 552.2 g/mol

³¹P{¹H} NMR (122 MHz, THF) δ (ppm) -9.3 (s, 3P).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 224.6 (s, CO), 170.5 (m, PC ring).

No resonance signal for the OH groups attached to the P₃C₃ is observed in the ¹H NMR spectrum, indicating that rapid exchange occurs on the NMR time scale.

E.A. [calc] for C₃₀H₆₃O₁₂P₃Mo (**Mo P₃C₃-H** + 6 ^tBuOH): C 44.78; H 7.89; E.A.[found]: C 44.63; H 7.93.

CCDC 2234734.

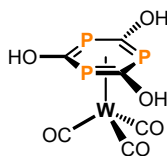
W P₃C₃-H

[WP₃C₃(OH)₃](CO)₃·x[tBuOH]₆

Yield: 8 mg (65%)

MF: C₁₂H₂₇O₁₂P₃W

MW: 640.1 g/mol



³¹P{¹H} NMR (202 MHz, CDCl₃): δ (ppm) = -14.9 (s, 3P, J_{W,P} = 16.4 Hz).

¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 214.2 (s, CO), 157.5 (s, ¹J_{CP} = 76.9 Hz, PC ring).

¹⁸³W NMR (203 MHz, THF-d₈): δ (ppm) -3110 (J_{W,P} = 19.5 Hz).

No resonance signal for the OH groups attached to the P₃C₃ is observed in the ¹H NMR spectrum, indicating that rapid exchange occurs on the NMR time scale.

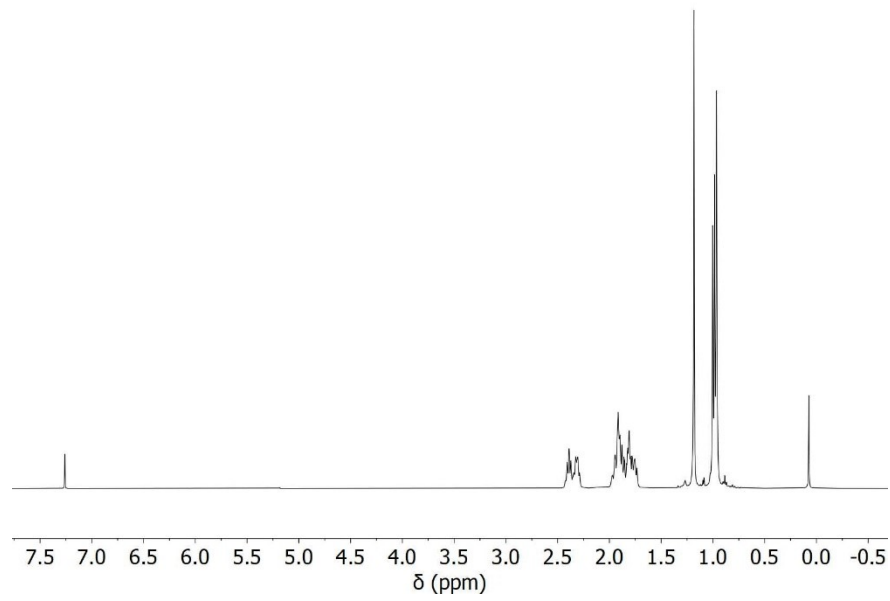
IR (cm⁻¹): 2975, 2865, 1987 (CO), 1920 (CO), 1461, 1366, 1068, 1033, 909.

E.A. [calc] for C₃₀H₆₃O₁₂P₃W (**W P₃C₃-H** + 6 ^tBuOH): C 40.37; H 7.12; E.A.[found]: C 40.12; H 7.22.

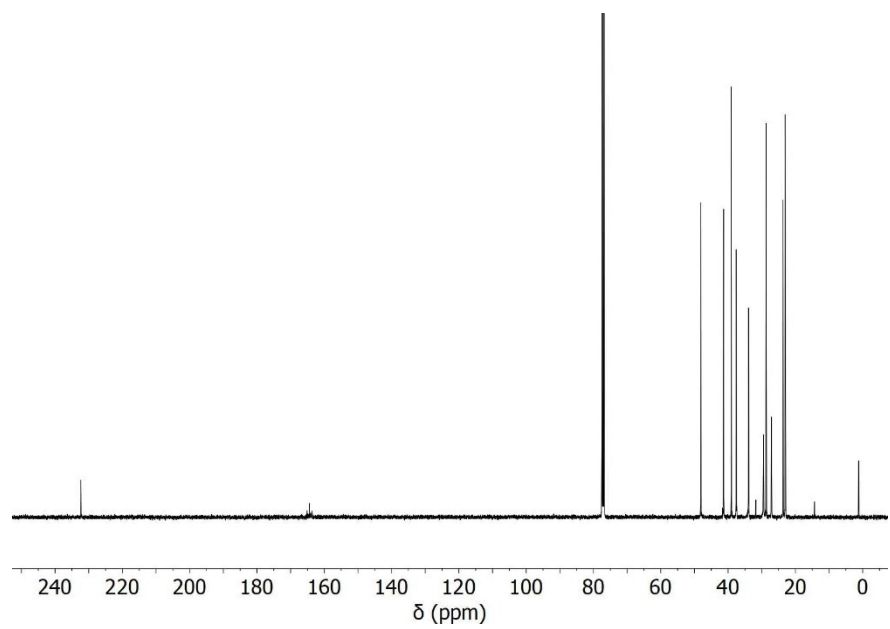
CCDC 2234729.

NMR Data

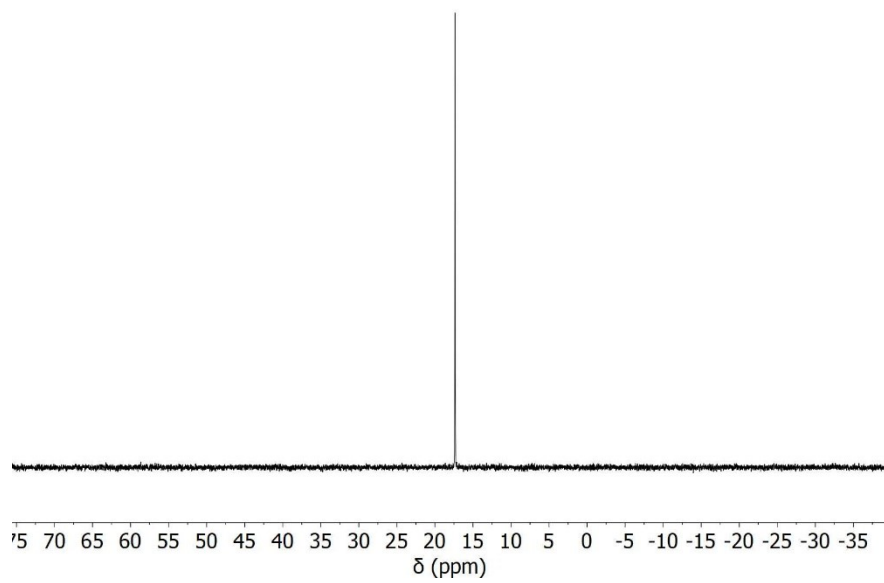
^1H NMR spectrum of $\text{Cr P}_3\text{C}_3\text{-B}$:



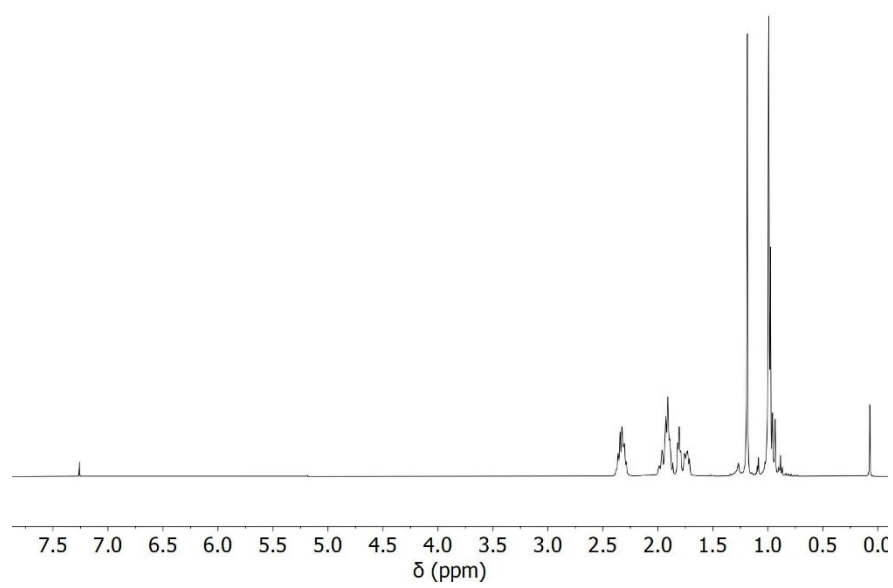
^{13}C $\{^1\text{H}\}$ NMR spectrum of $\text{Cr P}_3\text{C}_3\text{-B}$:



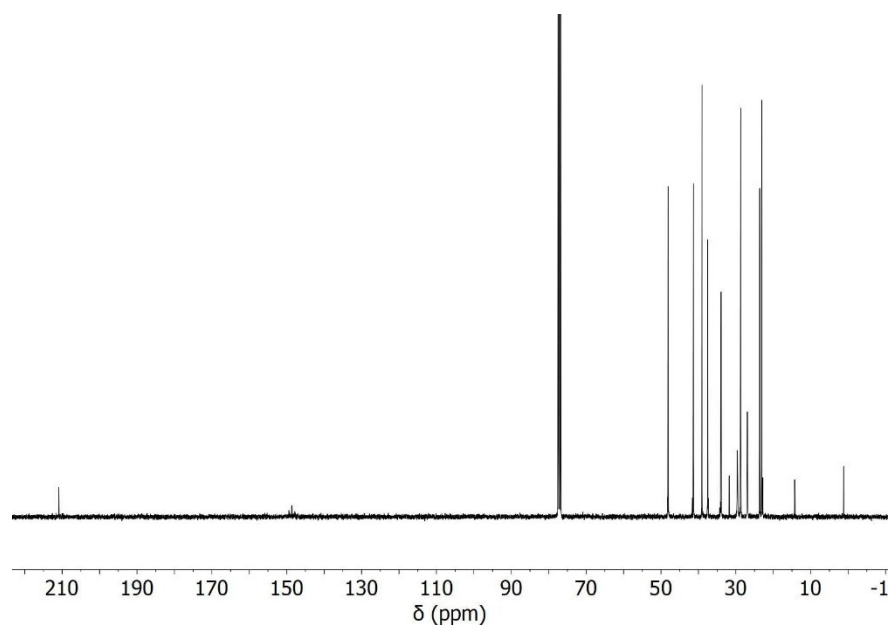
^{31}P $\{^1\text{H}\}$ NMR of **Cr** $\text{P}_3\text{C}_3\text{-B}$:



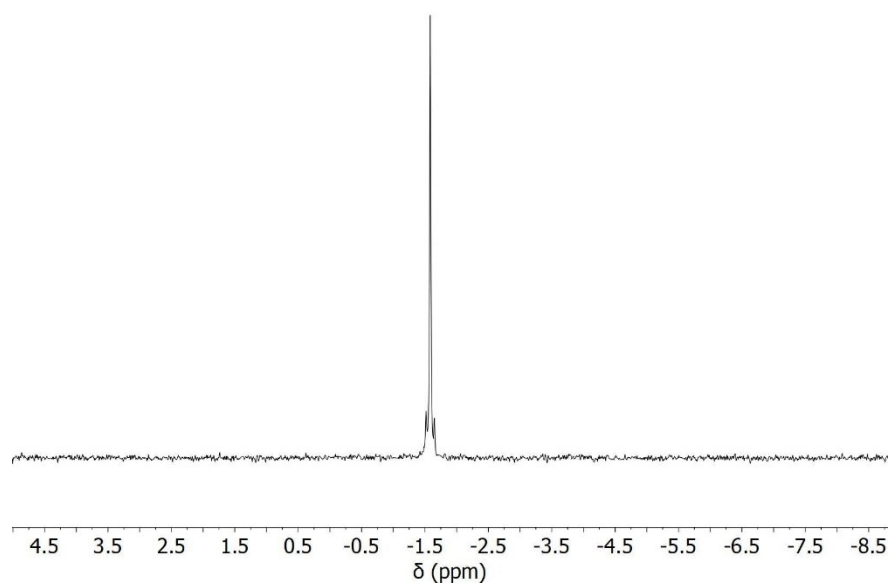
^1H NMR spectrum of **W** $\text{P}_3\text{C}_3\text{-B}$:



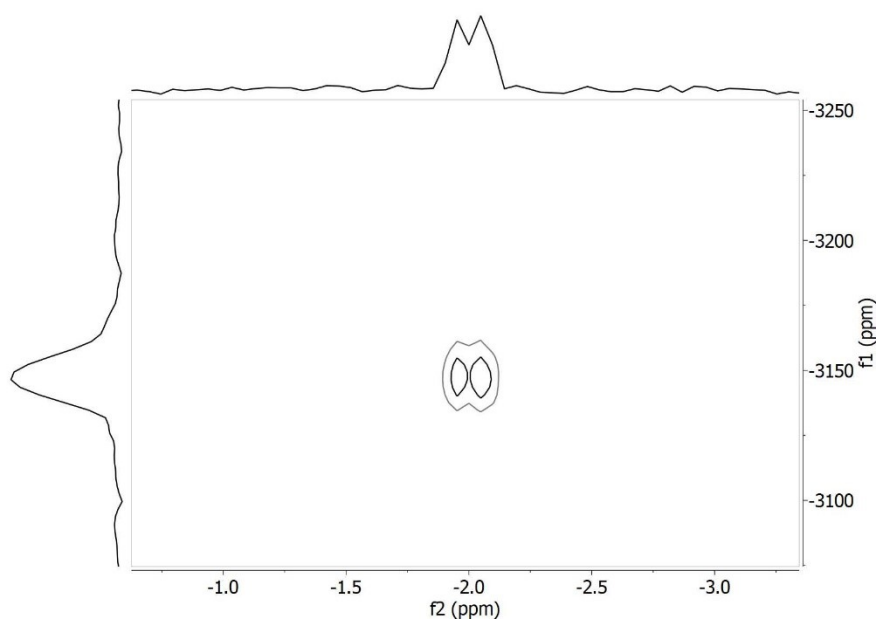
^{13}C $\{^1\text{H}\}$ NMR spectrum of **W** $\text{P}_3\text{C}_3\text{-B}$:



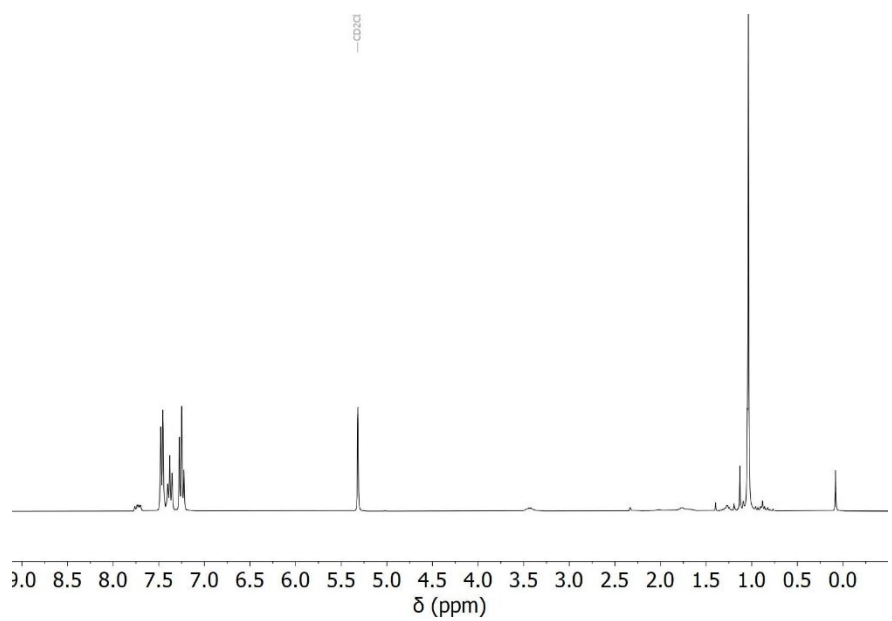
^{31}P $\{^1\text{H}\}$ NMR of **W** $\text{P}_3\text{C}_3\text{-B}$:



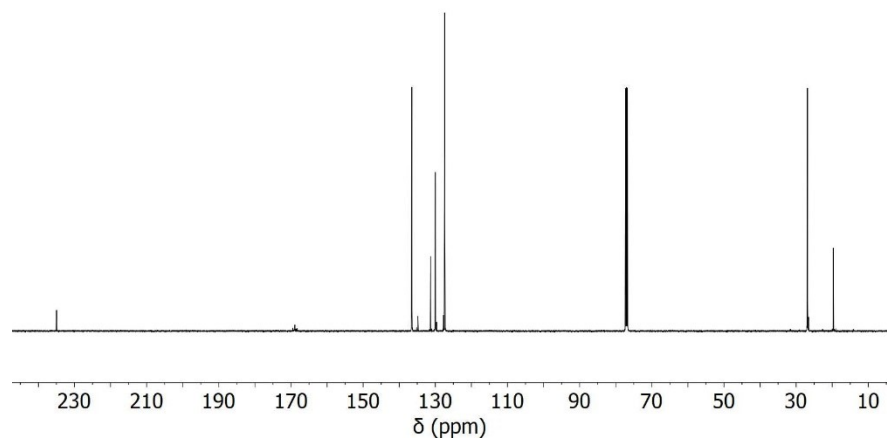
^{31}P - ^{183}W HSQC spectrum of **W** $\text{P}_3\text{C}_3\text{-B}$:



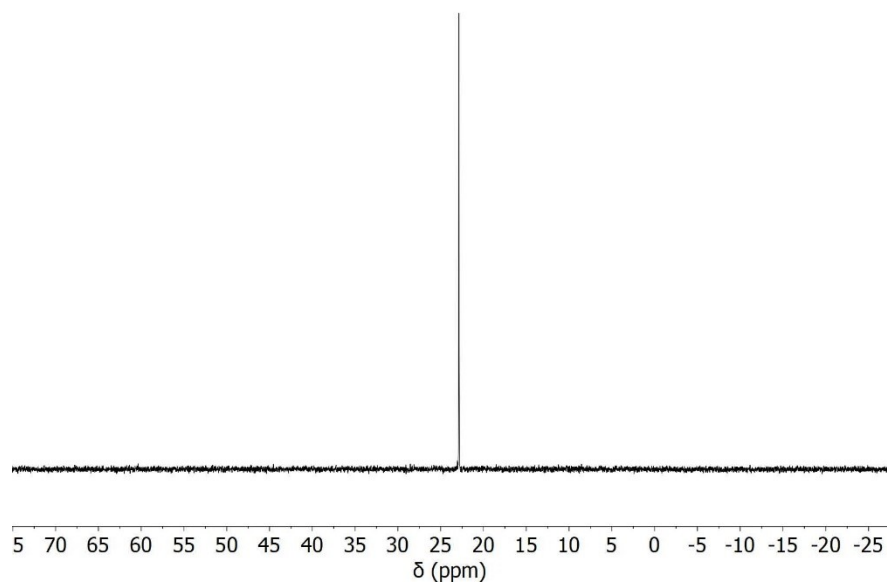
^1H NMR spectrum of **Cr** $\text{P}_3\text{C}_3\text{-Si}$:



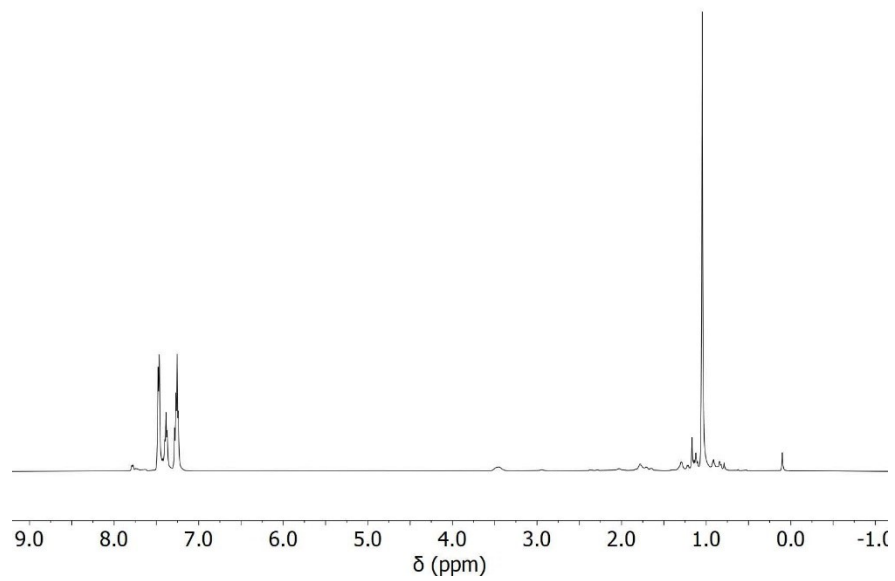
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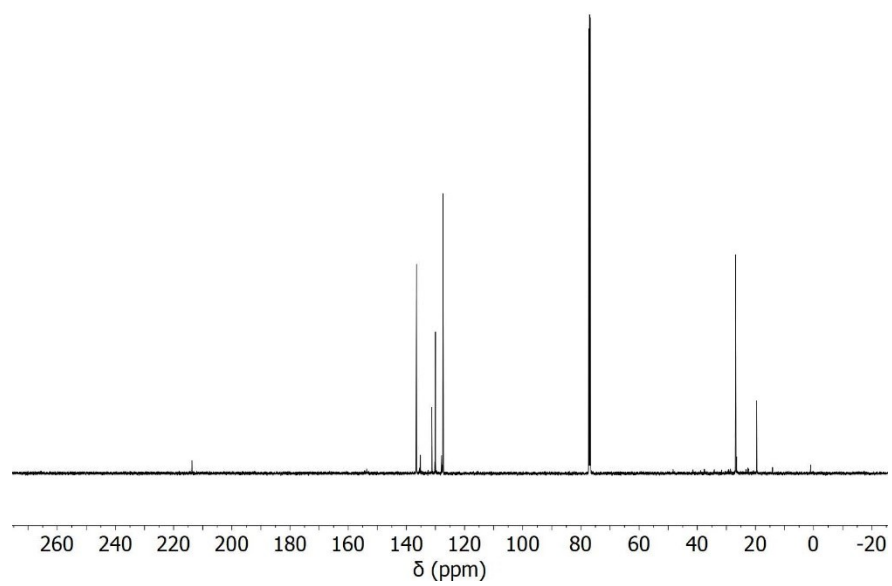
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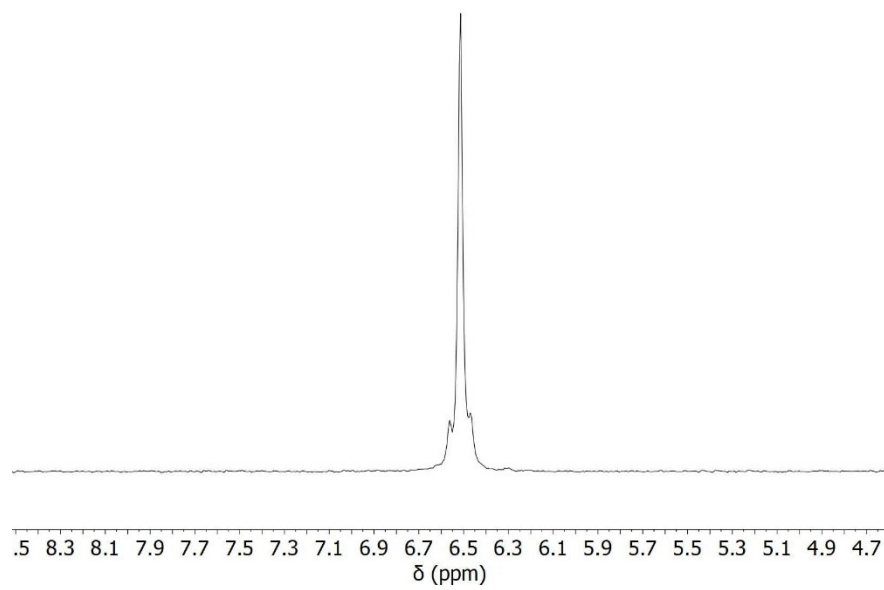
^1H NMR spectrum of **W** $\text{P}_3\text{C}_3\text{-Si}$:



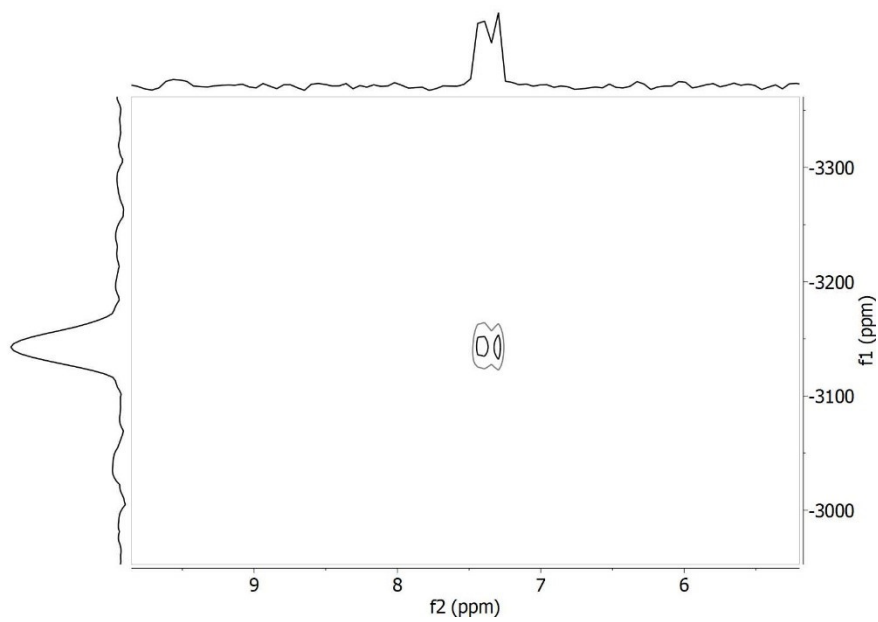
^{13}C $\{^1\text{H}\}$ NMR spectrum of **W** $\text{P}_3\text{C}_3\text{-Si}$:



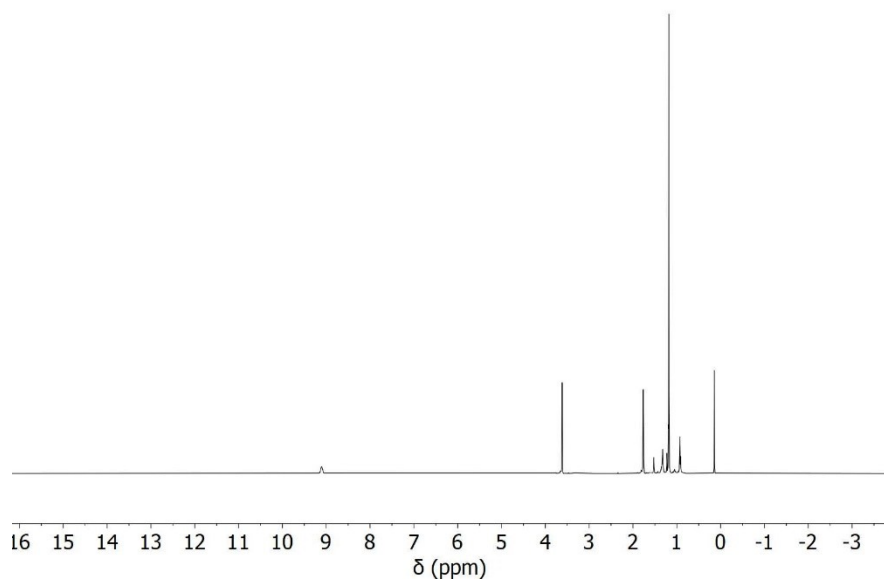
^{31}P $\{^1\text{H}\}$ NMR of $\text{W P}_3\text{C}_3\text{-Si}$:



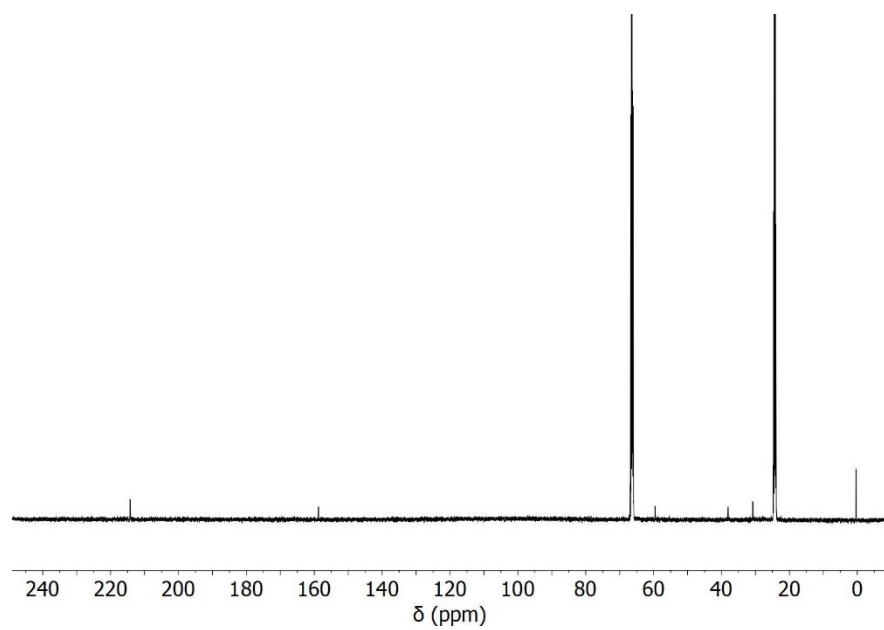
^{31}P - ^{183}W HSQC spectrum of $\text{W P}_3\text{C}_3\text{-Si}$:



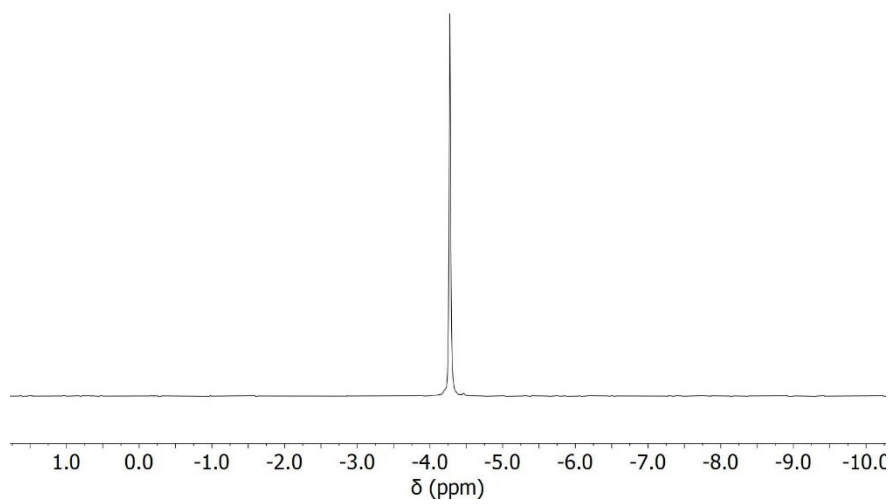
^1H NMR spectrum of $\text{Cr P}_3\text{C}_3\text{-H}$:



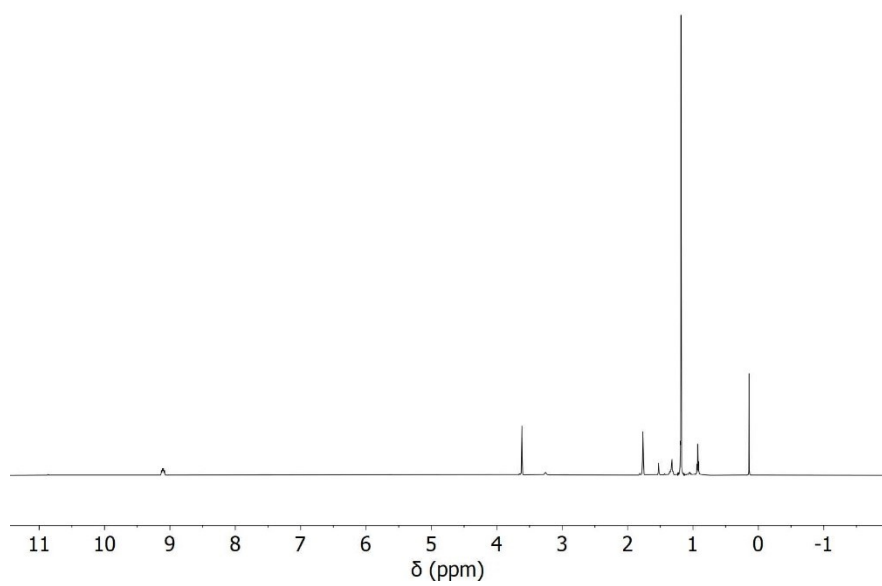
$^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of $\text{Cr P}_3\text{C}_3\text{-H}$:



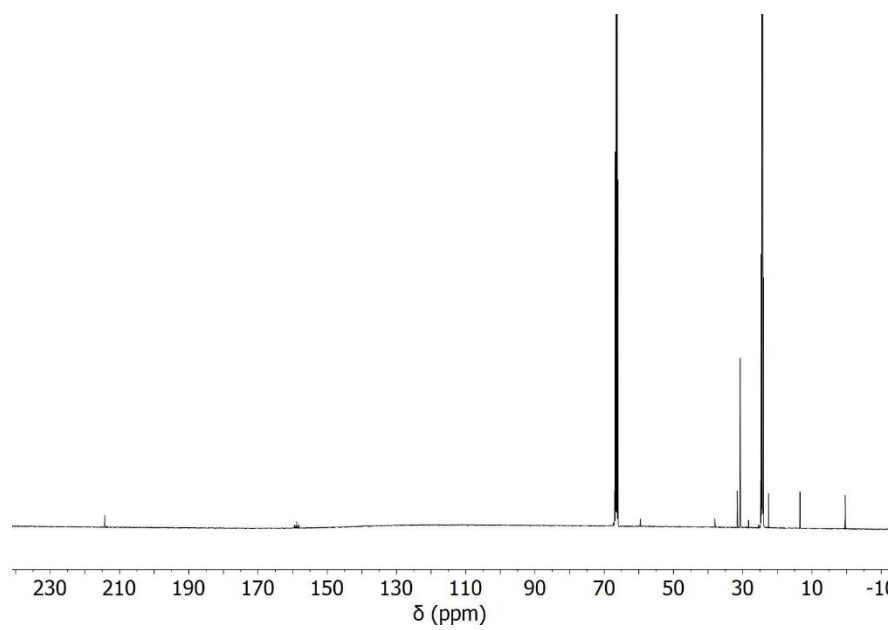
^{31}P $\{^1\text{H}\}$ NMR of $\text{Cr P}_3\text{C}_3\text{-H}$:



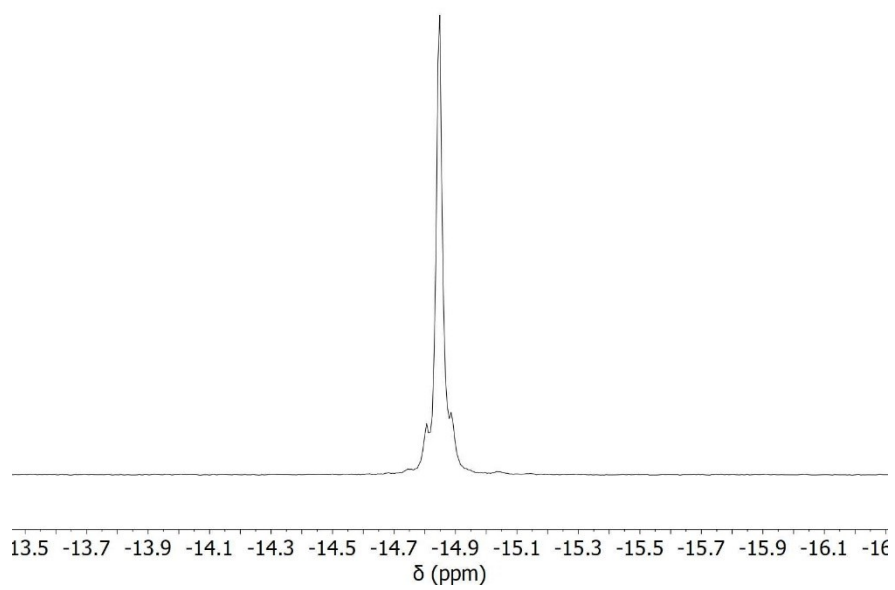
^1H NMR spectrum of $\text{W P}_3\text{C}_3\text{-H}$:



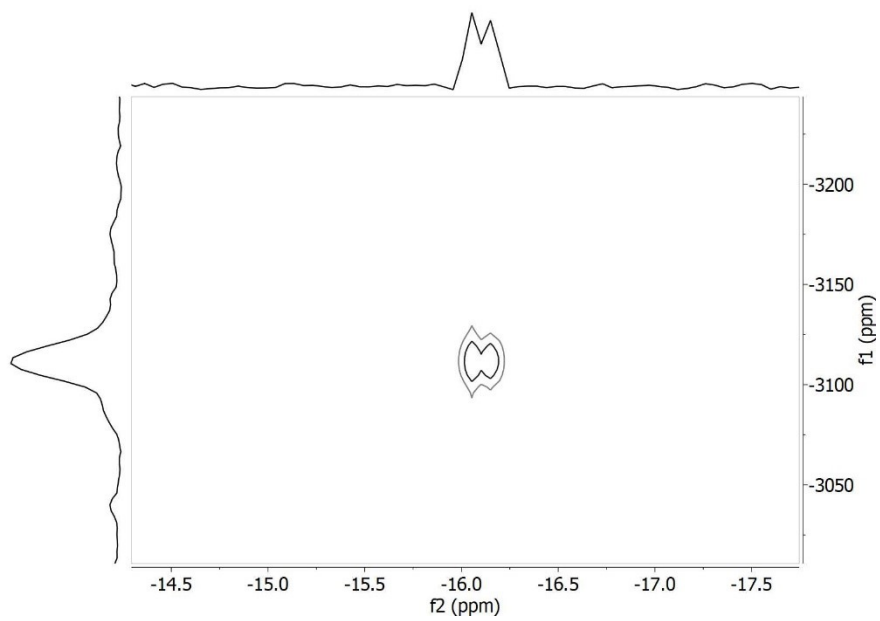
^{13}C $\{^1\text{H}\}$ NMR spectrum of **W** $\text{P}_3\text{C}_3\text{-H}$:



^{31}P $\{^1\text{H}\}$ NMR of **W** $\text{P}_3\text{C}_3\text{-H}$:

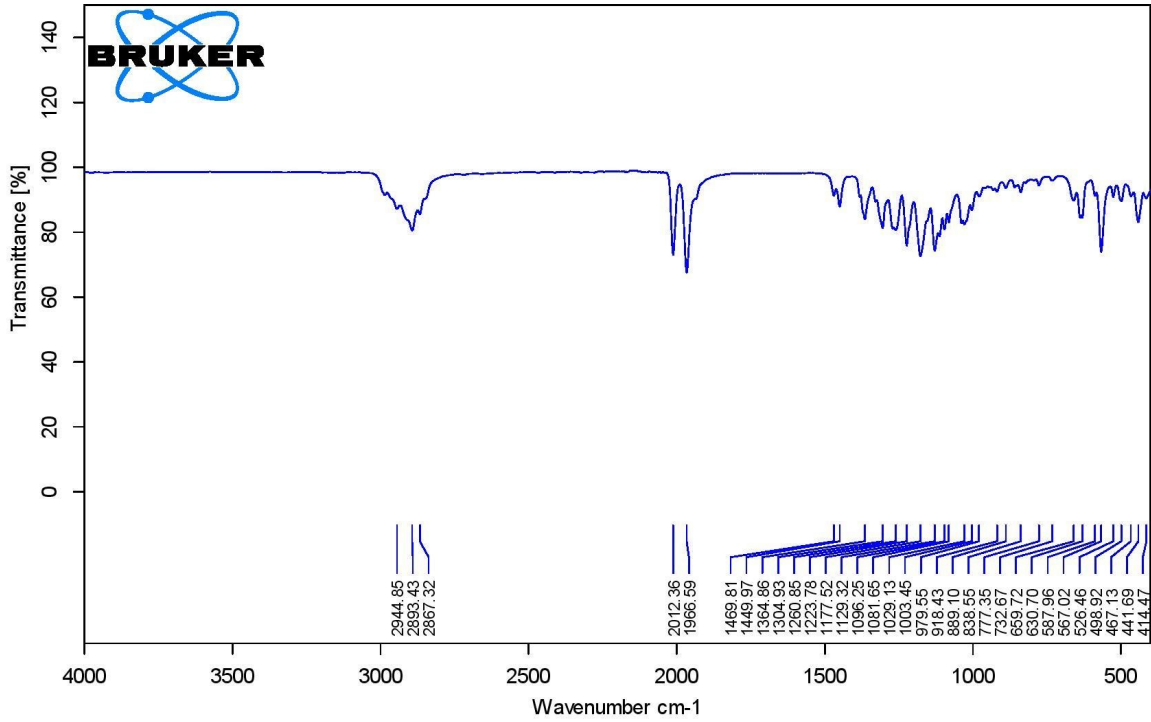


^{31}P - ^{183}W HSQC spectrum of $\text{W P}_3\text{C}_3\text{-H}$:

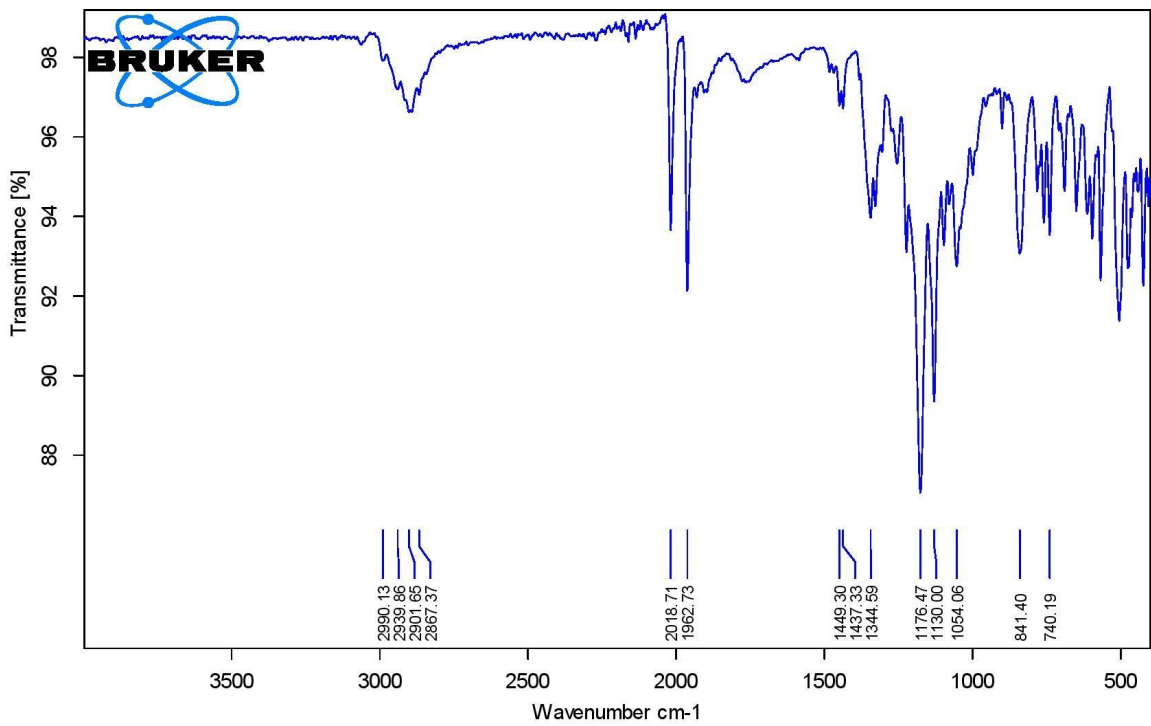


IR data

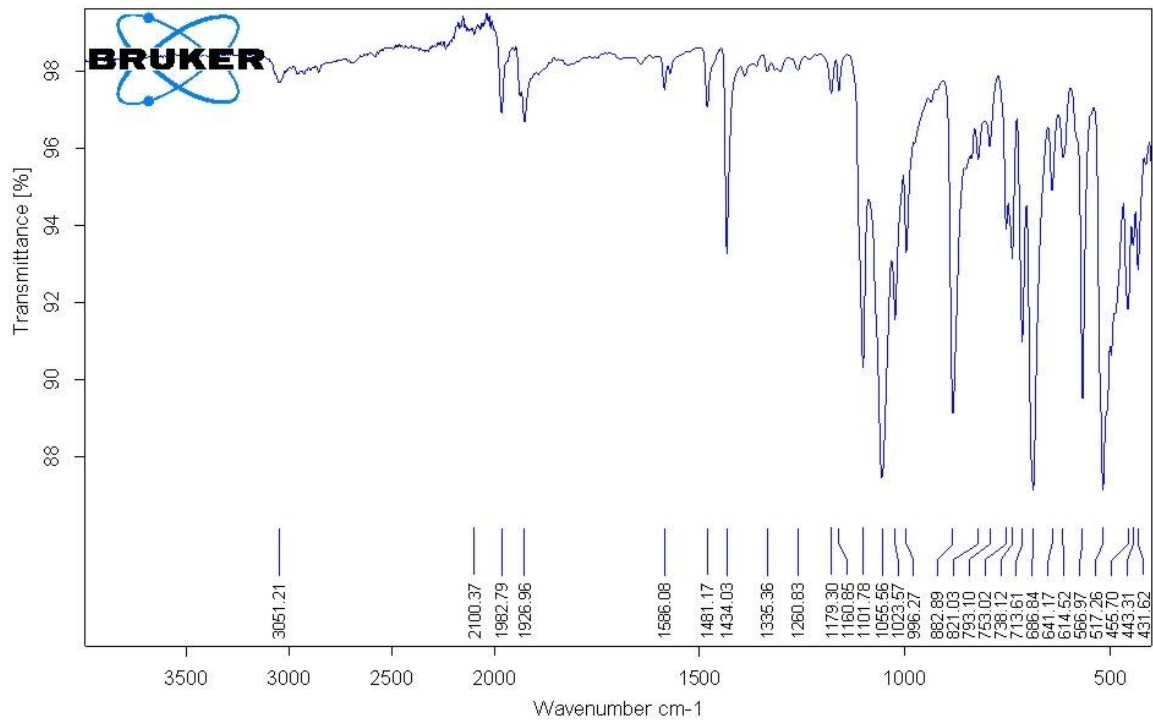
IR/ATR spectrum of Cr P₃C₃-B:



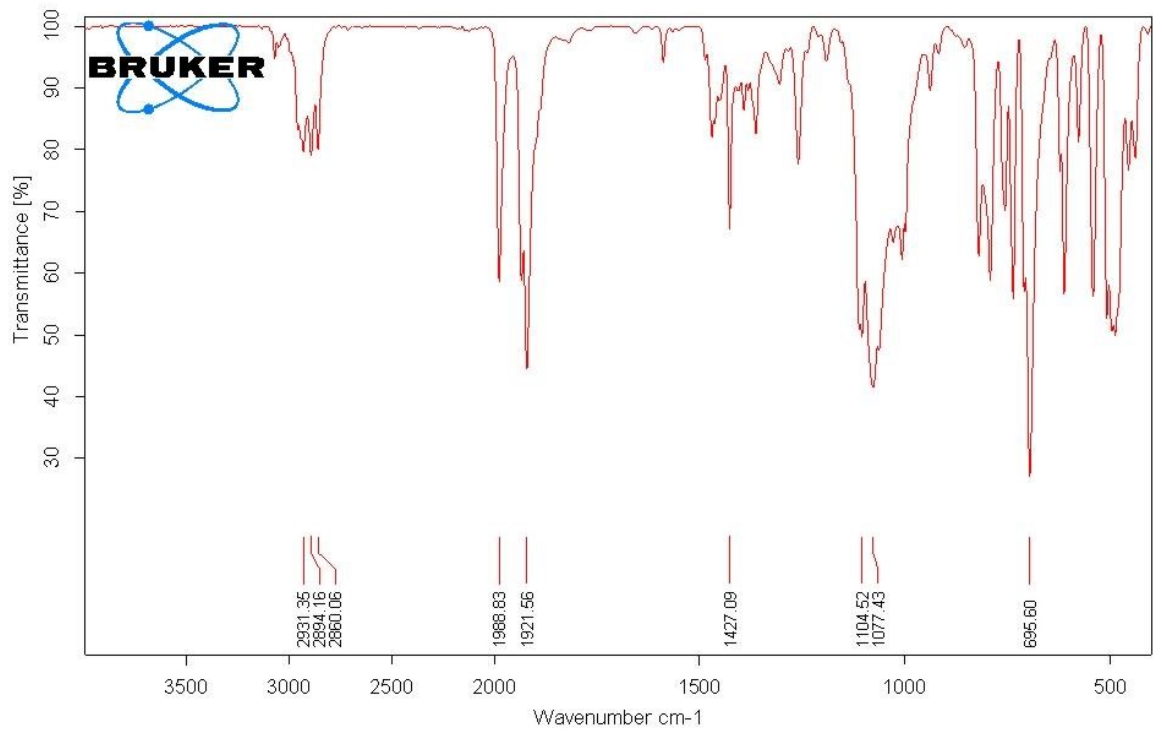
IR/ATR spectrum of W P₃C₃-B:



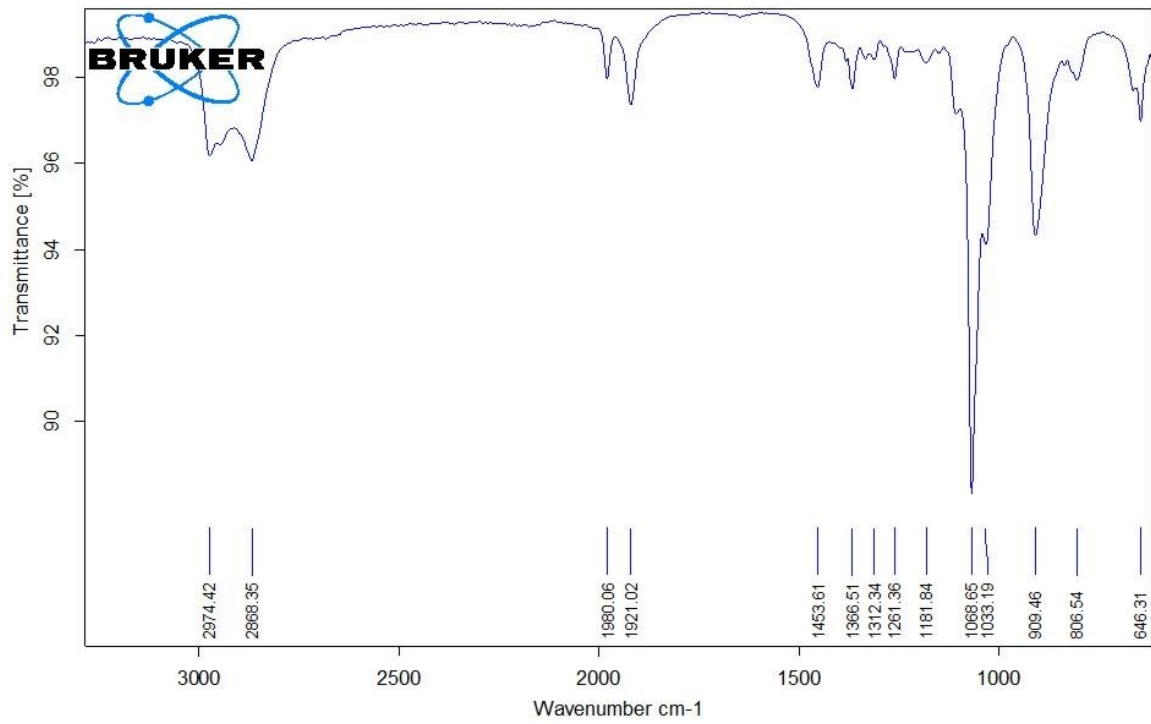
IR/ATR spectrum of Cr P₃C₃-Si:



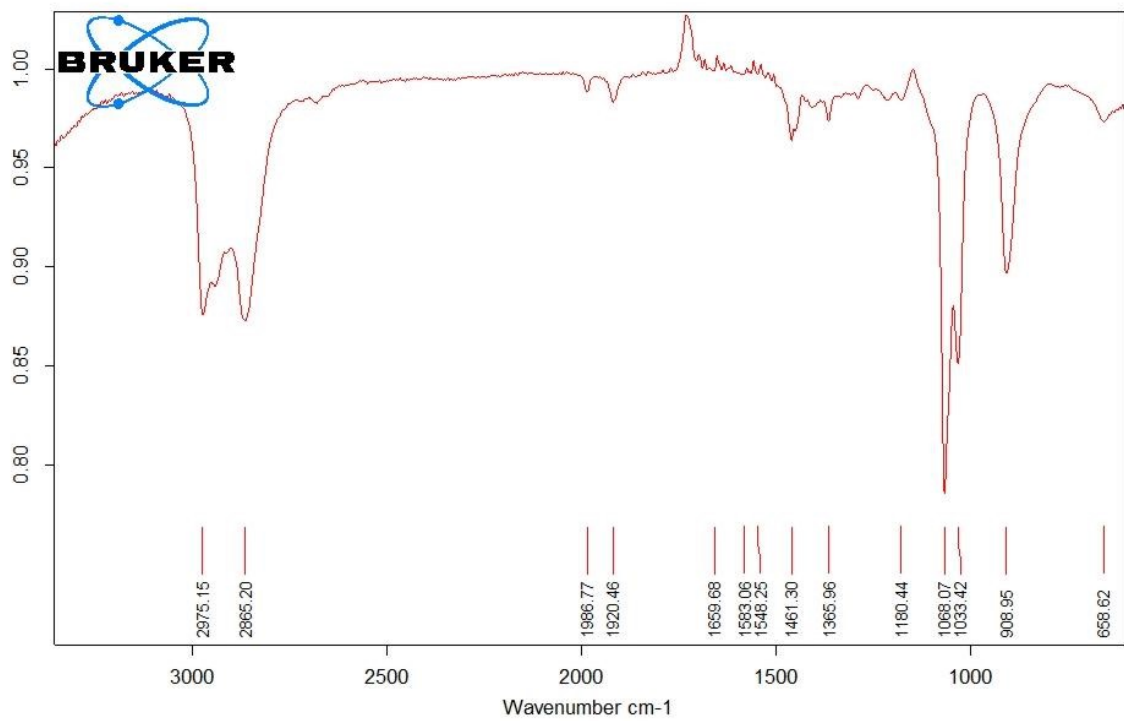
IR/ATR spectrum of W P₃C₃-Si:



IR/ATR spectrum of Cr P₃C₃-H:



IR/ATR spectrum of W P₃C₃-H:



Tables and figures

Figure 1 Trend between the J_{WP} and the M-ct bond distance of the tungsten triphosphinine complexes described in this work.

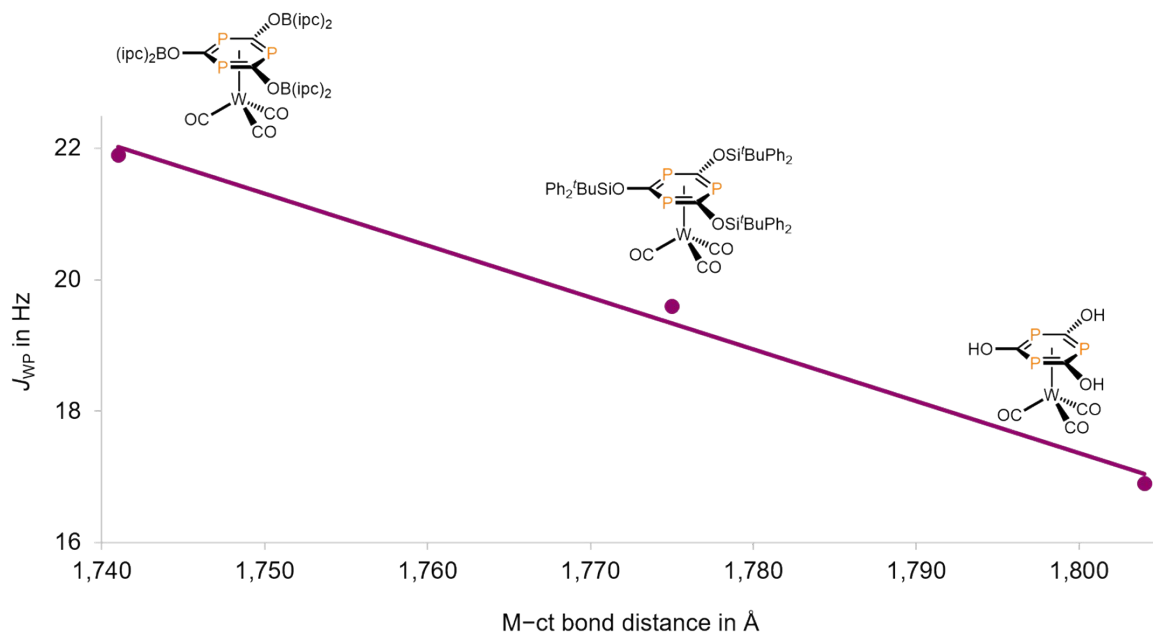
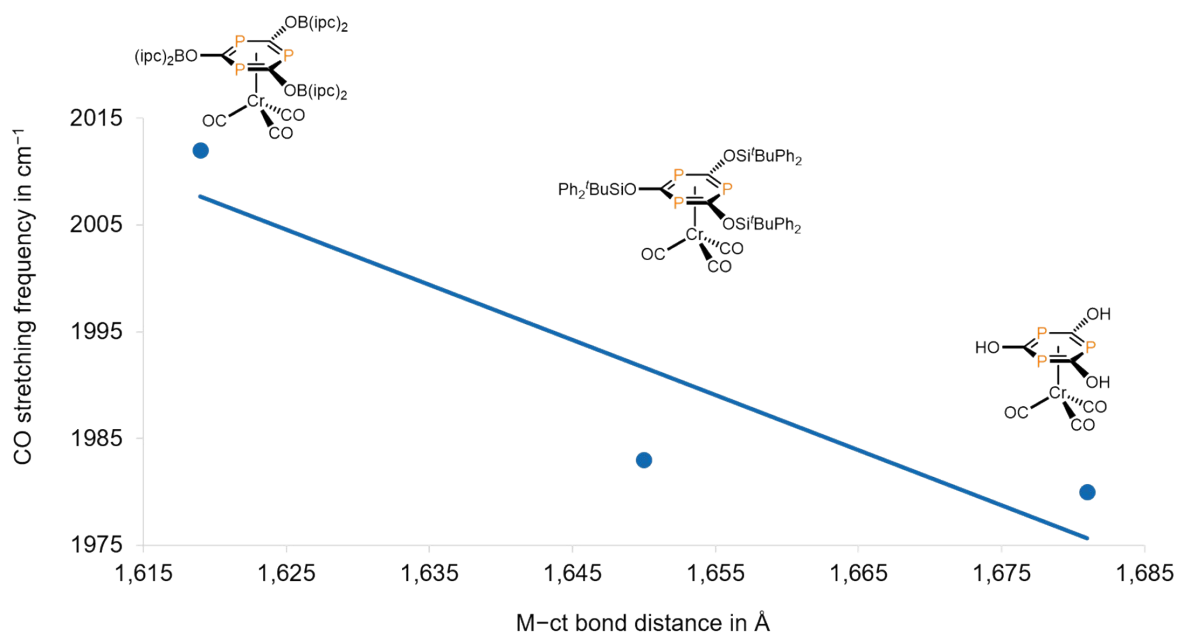


Figure 2 Trend between the CO stretching frequencies and the M-ct bond distance of the chromium triphosphinine complexes described in this work.



Crystallographic Data

Table 1 Crystal data and structure refinement for **Cr-P₃C₃-B** (CCDC 2234732).

Identification code	ASA_CrP3C3B3_2_0m
Empirical formula	C ₇₂ H ₁₁₆ B ₃ CrO ₆ P ₃
Formula weight	1254.98
Temperature/K	100.0
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	12.7561(3)
<i>b</i> /Å	21.5018(5)
<i>c</i> /Å	26.2809(6)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	7208.3(3)
<i>Z</i>	4
ρ_{calc} /cm ³	1.156
μ /mm ⁻¹	0.273
<i>F</i> (000)	2720.0
Crystal size/mm ³	0.412 × 0.357 × 0.216
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.45 to 60.854
Index ranges	-18 ≤ <i>h</i> ≤ 18, -30 ≤ <i>k</i> ≤ 29, -36 ≤ <i>l</i> ≤ 37
Reflections collected	104879
Independent reflections	21825 [<i>R</i> _{int} = 0.0557, <i>R</i> _{sigma} = 0.0523]
Data/restraints/parameters	21825/0/786
Goodness-of-fit on <i>F</i> ²	1.061
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0462, <i>wR</i> ₂ = 0.0941
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0588, <i>wR</i> ₂ = 0.0995
Largest diff. peak/hole / e Å ⁻³	0.56/-0.30
Flack parameter	-0.133(5)

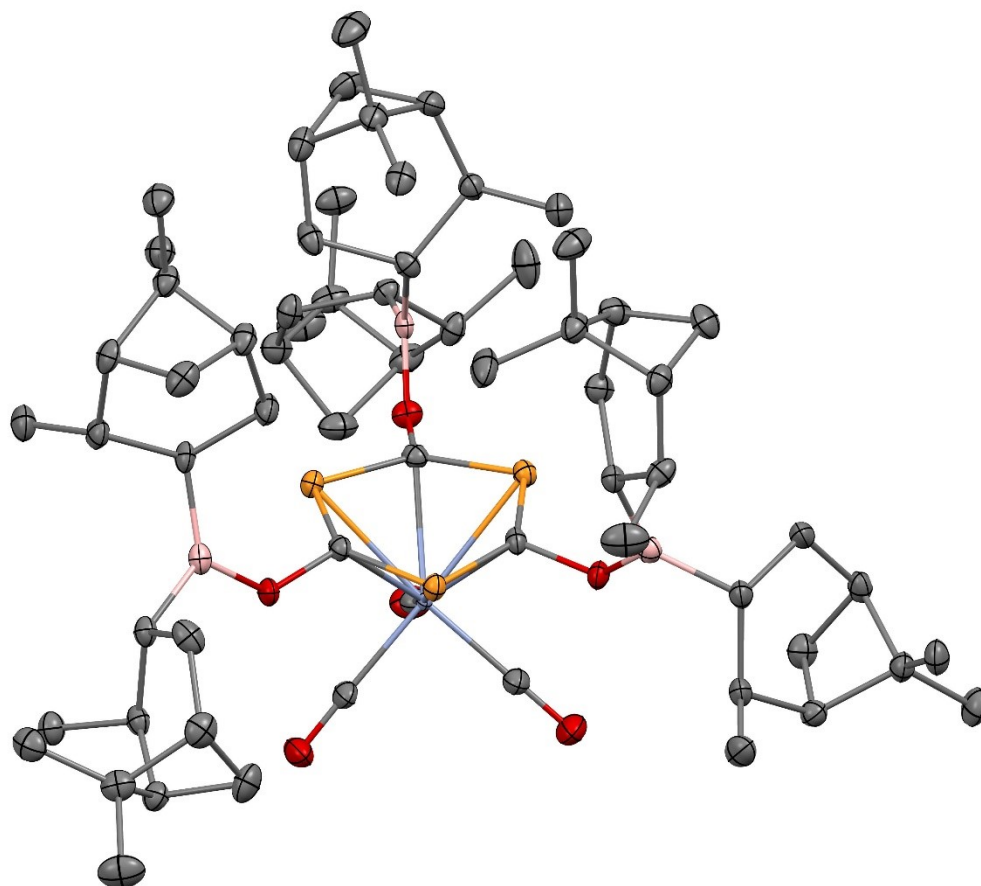


Figure 1: view of **Cr-P₃C₃-B** with displacement ellipsoids at 50 % probability level. Cr is shown in blue, P in orange, C in dark grey, O in red and B in pink. For clarity all hydrogen atoms and a solvent molecule n-hexane were omitted.

Table 2 Crystal data and structure refinement for **W-P₃C₃-B** (CCDC 2234733).

Identification code	cu_ASA_WP3C3B3_0m
Empirical formula	C ₂₆₄ H ₄₀₈ B ₁₂ O ₂₄ P ₁₂ W ₄
Formula weight	5202.64
Temperature/K	100.00
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a/Å	11.9699(3)
b/Å	22.1826(6)
c/Å	27.2092(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	7224.7(3)
Z	1
ρ _{calc} /g/cm ³	1.196
μ/mm ⁻¹	3.925
F(000)	2720.0
Crystal size/mm ³	0.211 × 0.093 × 0.059
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.14 to 149.258
Index ranges	-13 ≤ h ≤ 14, -27 ≤ k ≤ 26, -33 ≤ l ≤ 34
Reflections collected	95733
Independent reflections	14746 [R _{int} = 0.0422, R _{sigma} = 0.0269]
Data/restraints/parameters	14746/171/812
Goodness-of-fit on F ²	1.128
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0265, wR ₂ = 0.0648
Final R indexes [all data]	R ₁ = 0.0268, wR ₂ = 0.0649
Largest diff. peak/hole / e Å ⁻³	1.11/-0.68
Flack parameter	-0.006(3)

Table 3 Crystal data and structure refinement for **Cr-P₃C₃-Si** (CCDC 2234730).

Identification code	ASA_CrP3C3SiR3_ASAWP3C3SiR3_1_0m
Empirical formula	C ₅₄ H ₅₇ CrO ₆ P ₃ Si ₃
Formula weight	1031.17
Temperature/K	100.0
Crystal system	orthorhombic
Space group	<i>Pbca</i>
a/Å	11.2421(2)
b/Å	28.2246(6)
c/Å	33.9555(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	10774.2(4)
Z	8
ρ _{calc} /g/cm ³	1.271
μ/mm ⁻¹	3.606
F(000)	4320.0
Crystal size/mm ³	0.42 × 0.06 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.204 to 144.864
Index ranges	-13 ≤ h ≤ 13, -34 ≤ k ≤ 28, -41 ≤ l ≤ 41
Reflections collected	79710
Independent reflections	10644 [R _{int} = 0.0518, R _{sigma} = 0.0275]
Data/restraints/parameters	10644/0/613
Goodness-of-fit on F ²	1.036
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0301, wR ₂ = 0.0712
Final R indexes [all data]	R ₁ = 0.0388, wR ₂ = 0.0774
Largest diff. peak/hole / e Å ⁻³	0.34/-0.26

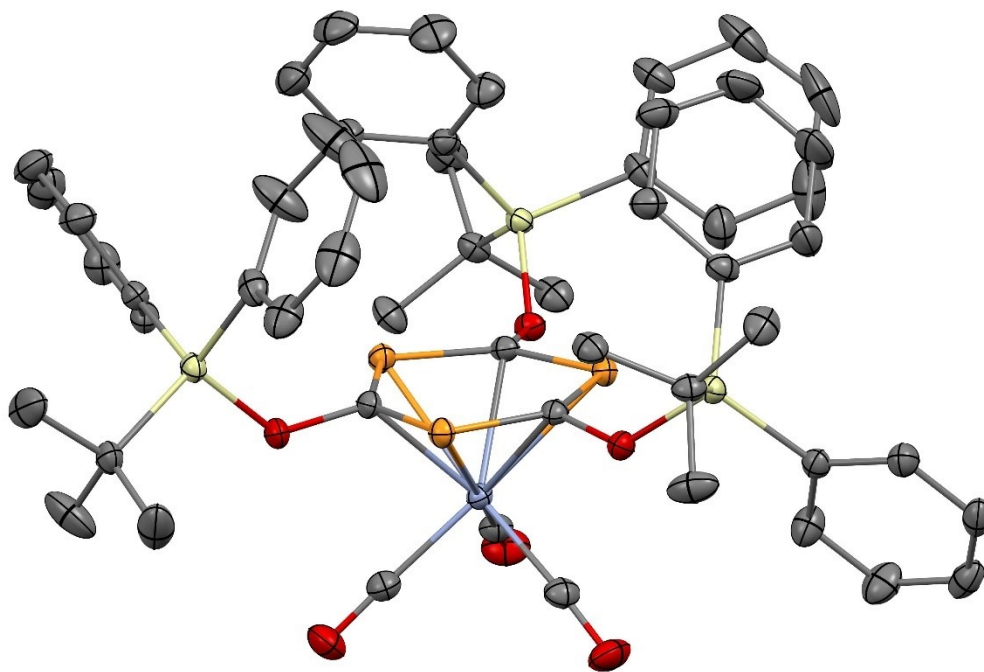


Figure 3: view of $\text{Cr-P}_3\text{C}_3\text{-Si}$ with displacement ellipsoids at 50 % probability level. Cr is shown in blue, P in orange, C in dark grey, O in red and Si in yellow. For clarity all hydrogen atoms were omitted.

Table 4 Crystal data and structure refinement for **W-P₃C₃-Si** (CCDC 2234735).

Identification code	ASA_WP3C3Si3_Cu_auto
Empirical formula	C ₁₆₂ H ₁₇₁ O ₁₈ P ₉ Si ₉ W ₃
Formula weight	3489.07
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	<i>Pbca</i>
a/Å	11.26200(10)
b/Å	28.2147(2)
c/Å	34.1306(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	10845.13(14)
Z	2.666667
ρ _{calc} /g/cm ³	1.425
μ/mm ⁻¹	5.795
F(000)	4720.0
Crystal size/mm ³	0.321 × 0.042 × 0.029
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.78 to 160.842
Index ranges	-14 ≤ h ≤ 14, -36 ≤ k ≤ 35, -43 ≤ l ≤ 37
Reflections collected	79808
Independent reflections	11757 [R _{int} = 0.0488, R _{sigma} = 0.0298]
Data/restraints/parameters	11757/0/613
Goodness-of-fit on F ²	1.078
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0289, wR ₂ = 0.0744
Final R indexes [all data]	R ₁ = 0.0335, wR ₂ = 0.0766
Largest diff. peak/hole / e Å ⁻³	1.06/-0.97

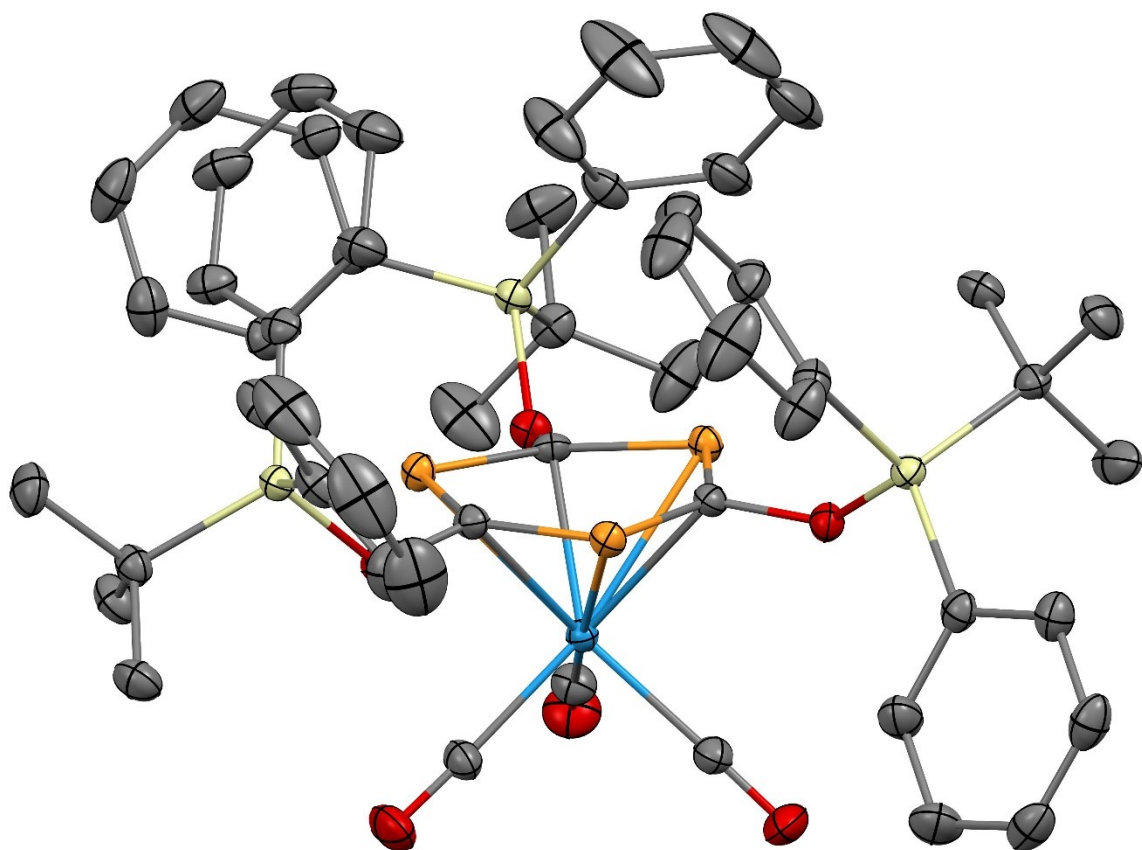


Figure 4: view of $W-P_3C_3-Si$ with displacement ellipsoids at 50 % probability level. W is shown in blue, P in orange, C in dark grey, O in red and Si in yellow. For clarity all hydrogen atoms were omitted.

Table 5 Crystal data and structure refinement for **Cr-P₃C₃-H** (CCDC 2234731).

Identification code	ASA_CrOH_1_0m
Empirical formula	C ₃₀ H ₆₃ CrO ₁₂ P ₃
Formula weight	760.71
Temperature/K	99.99
Crystal system	trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	16.0104(10)
<i>b</i> /Å	16.0104(10)
<i>c</i> /Å	86.122(5)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	19118(3)
<i>Z</i>	18
ρ_{calc} /g/cm ³	1.189
μ /mm ⁻¹	0.432
<i>F</i> (000)	7344.0
Crystal size/mm ³	0.455 × 0.294 × 0.213
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	1.418 to 54.74
Index ranges	-20 ≤ <i>h</i> ≤ 20, -20 ≤ <i>k</i> ≤ 20, -110 ≤ <i>l</i> ≤ 110
Reflections collected	94876
Independent reflections	9634 [<i>R</i> _{int} = 0.0694, <i>R</i> _{sigma} = 0.0386]
Data/restraints/parameters	9634/36/473
Goodness-of-fit on <i>F</i> ²	1.032
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.1025
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0686, <i>wR</i> ₂ = 0.1167
Largest diff. peak/hole / e Å ⁻³	0.82/-0.44

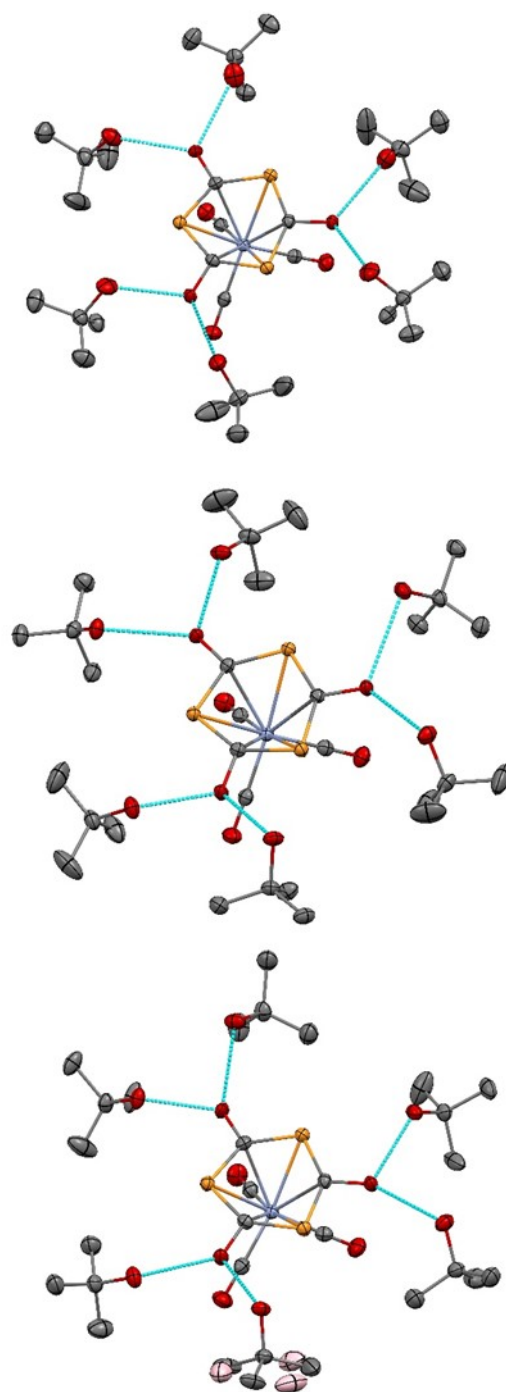


Figure 5: view of the three crystallographically independent molecules $\text{Cr-P}_3\text{C}_3\text{-H}$ with displacement ellipsoids at 50 % probability level. The Cr is shown in blue, P in orange, C in dark grey and O in red. The *t*-butanol molecules forming hydrogen bonds to the OH-groups are shown as well. The less occupied split positions of disordered atoms are shown in pink. For clarity all hydrogen atoms were omitted.

Table 6: Crystal data and structure refinement for **Mo-P₃C₃-H** (CCDC 2234734).

Identification code	ASA_MoP3C3OH3_4_0m
Empirical formula	C ₃₀ H ₆₃ MoO ₁₂ P ₃
Formula weight	804.65
Temperature/K	100.0
Crystal system	trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	16.0345(8)
<i>b</i> /Å	16.0345(8)
<i>c</i> /Å	86.937(5)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	19357(2)
<i>Z</i>	18
ρ_{calc} /g/cm ³	1.242
μ /mm ⁻¹	0.465
<i>F</i> (000)	7668.0
Crystal size/mm ³	0.2 × 0.15 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.216 to 50.69
Index ranges	-19 ≤ <i>h</i> ≤ 19, -18 ≤ <i>k</i> ≤ 19, -104 ≤ <i>l</i> ≤ 104
Reflections collected	58574
Independent reflections	7899 [<i>R</i> _{int} = 0.0480, <i>R</i> _{sigma} = 0.0244]
Data/restraints/parameters	7899/140/478
Goodness-of-fit on <i>F</i> ²	1.125
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0637, <i>wR</i> ₂ = 0.1629
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0687, <i>wR</i> ₂ = 0.1663
Largest diff. peak/hole / e Å ⁻³	6.31/-0.87

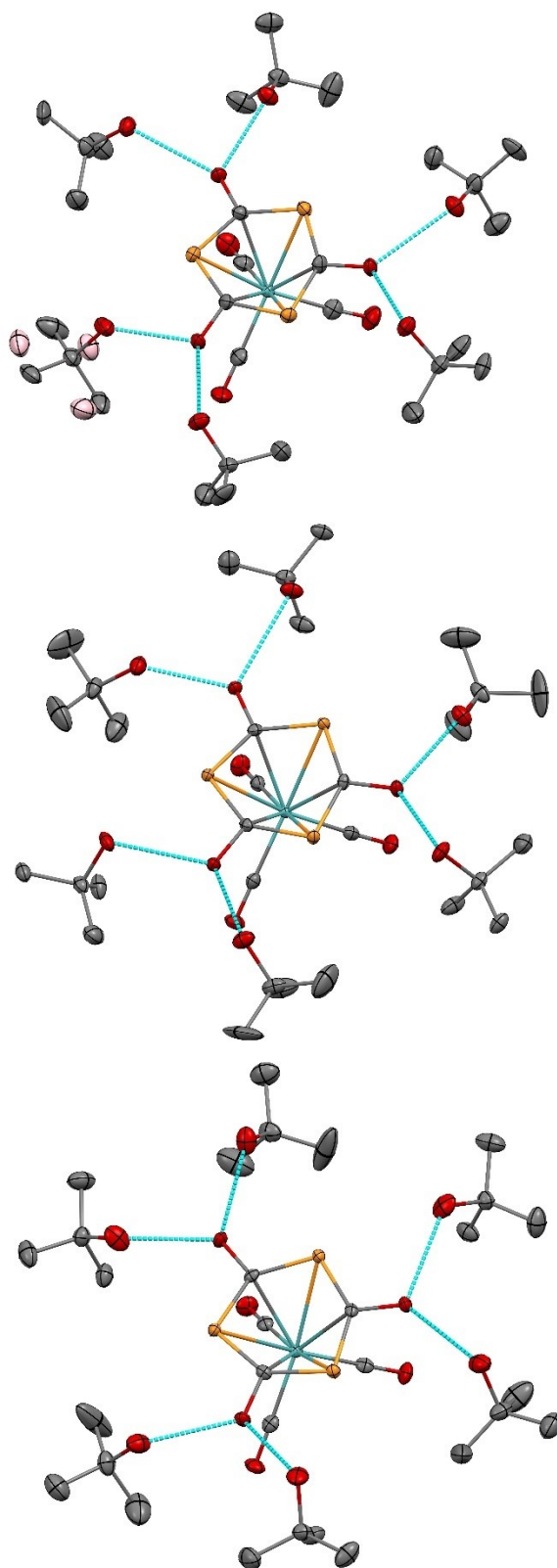


Figure 6: view of the three crystallographically independent molecules **Mo-P₃C₃-H** with displacement ellipsoids at 50 % probability level. The Mo is shown in blue, P in orange, C in dark grey and O in red. The *t*-butanol molecules forming hydrogen bonds to the OH-groups are shown as well. The less occupied split positions of disordered atoms are shown in pink. For clarity all hydrogen atoms were omitted.

Table 7: Crystal data and structure refinement for **W-P₃C₃-H** (CCDC 2234729).

Identification code	ASA_WOH_1_1_0m
Empirical formula	C ₃₀ H ₆₃ O ₁₂ P ₃ W
Formula weight	892.56
Temperature/K	100.0
Crystal system	trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	15.9824(13)
<i>b</i> /Å	15.9824(13)
<i>c</i> /Å	29.381(3)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	6499.6(12)
<i>Z</i>	6
ρ_{calc} /cm ³	1.368
μ /mm ⁻¹	2.825
<i>F</i> (000)	2748.0
Crystal size/mm ³	0.21 × 0.201 × 0.108
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.098 to 51.036
Index ranges	-19 ≤ <i>h</i> ≤ 17, -1 ≤ <i>k</i> ≤ 19, -35 ≤ <i>l</i> ≤ 35
Reflections collected	2688
Independent reflections	2688 [<i>R</i> _{int} = 0.0742, <i>R</i> _{sigma} = 0.0370]
Data/restraints/parameters	2688/140/148
Goodness-of-fit on <i>F</i> ²	1.087
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0682, <i>wR</i> ₂ = 0.1476
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0921, <i>wR</i> ₂ = 0.1700
Largest diff. peak/hole / e Å ⁻³	7.14/-3.27

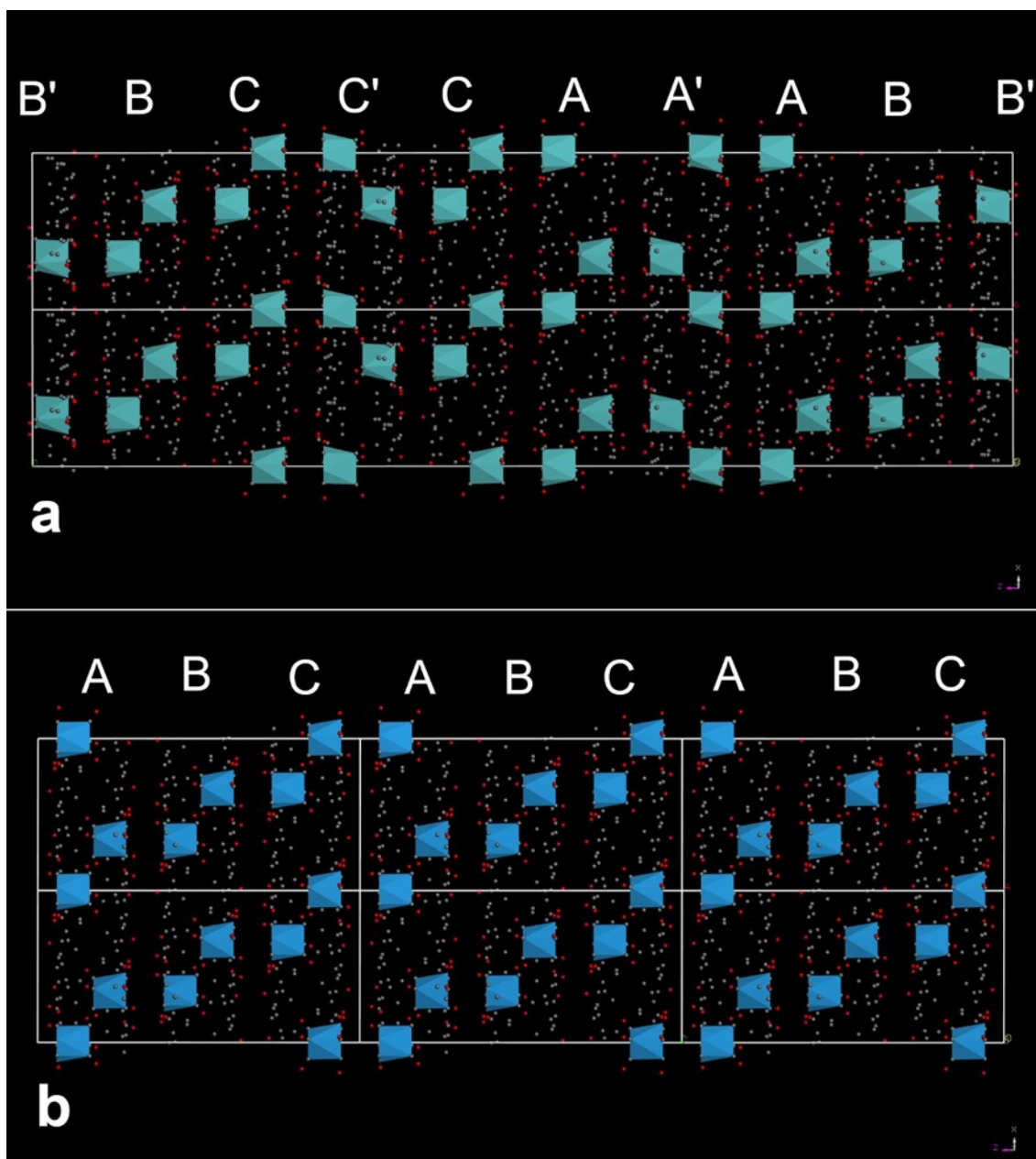


Figure 8: Projections of the crystal structures of **Mo**-P₃C₃-H (a) and **W**-P₃C₃-H (b) along the b-axis, showing the layer stacking sequences along the c-axis (horizontal) and the similarity between both crystal structures. **Cr**-P₃C₃-H is isotypic to **Mo**-P₃C₃-H. Hydrogen atoms are omitted for clarity. The different layers are marked with capital letters ABC while A'B'C' denote ABC-layers related by an inversion. While **W**-P₃C₃-H has a stacking sequence of ABC, **Mo**-P₃C₃-H has a more complicated stacking sequence of B'BCC'CAA'AB, leading to a tripling of the c-axis compared to **W**-P₃C₃-H. In **Mo**-P₃C₃-H and **W**-P₃C₃-H the occurrence of stacking faults leads to significant residual electron density peaks on lines parallel to the c-axis and running through 0 0 0, 1/3 2/3 0 and 2/3 1/3 0.

Computations

The computations were carried out with the Gaussian 09 package.²

The geometries were optimized and then frequency calculations were performed. The B3LYP functional combined with the 6-311+G** basis set was already used for similar molecules.¹

Table S8: Kohn-Sham energies

Molecule	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap (eV)
benzene ¹	-7.08	-0.45	6.60
phosphinine	-6.93	-1.70	5.23
1,3 diphosphinine	-7.14	-2.25	4.88
1,3,5 triphosphinine ¹	-7.31	-2.68	4.63
trihydroxi triphosphinine ¹	-6.58	-2.31	4.27

XYZ coordinates and total energies

Phosphinine

E=-534.955277

C 0.368170 -1.335710 -0.000026

C -1.018323 -1.224935 -0.000006

C -1.687104 -0.000257 0.000011

C -1.018070 1.224962 0.000006

C 0.367900 1.335986 0.000000

H 0.801534 2.332017 -0.000084

P 1.488002 -0.000023 0.000010

H -1.614042 2.133555 -0.000023

H -2.771720 0.000240 0.000013

H -1.613354 -2.134126 0.000006

H 0.802108 -2.331603 0.000017

1,3 Diphosphinine

E=-837.59952

C -0.000084 -1.343928 -0.000072

P -1.582740 -0.630731 -0.000006
C -1.241046 1.077494 0.000018
C 0.000077 1.709789 0.000002
C 1.241249 1.077457 0.000009
H 2.119262 1.717780 -0.000047
P 1.582670 -0.631008 0.000005
H 0.000535 2.798307 -0.000026
H -2.119381 1.717402 0.000045
H -0.000542 -2.432285 0.000290

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1. R. Suter, Y. Mei, M. Baker, Z. Benkó, Z. Li and H. Grützmacher, *Angewandte Chemie International Edition*, 2017, **56**, 1356-1360.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09* (Gaussian, Inc., Wallingford CT, 2009).