Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Zero-valent metals in metal-organic frameworks: *fac*-M(CO)$_3$(pyrazine)$_{3/2}$

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Synthesis

All chemicals and solvents were used as received from Sigma-Aldrich®. Reaction products were stored under argon gas.

Synthesis of **Cr**: In an oven-dried ampoule ($V = 21$ mL) were placed $Cr(CO)_6$ (100 mg, 0.454 mmol) and pyz (1.0 g, 12.5 mmol). The ampoule was evacuated for 2 min to remove all oxygen and afterwards flame sealed. The ampoule was inserted into a furnace and the temperature was ramped to 170°C over the course of 4 h. The ampoule was left at 170°C for 40 h and afterwards cooled to room temperature over 16 h. The dark shiny product was washed with acetonitrile (100 mL) to remove excess pyz and residual $Cr(CO)_6$. Yield: 18 mg (13% based on Cr). Calculated (experimental) elemental analysis for $C_9CrH_6N_3O_3{\cdot}C_2H_2N$: C 44.60% (44.35%), H 2.72% (2.72%), N 18.92% (18.72%), Cr 17.55% (17.41%).

Synthesis of **Mo**: In an oven-dried ampoule ($V = 21$ mL) were placed $Mo(CO)_6$ (80 mg, 0.30 mmol) and pyz (1.25 g, 15.6 mmol). The ampule was evacuated for 2 min to remove all oxygen and afterwards flame sealed. The ampule was inserted into a furnace and the temperature ramped to 150°C over the course of 4 h. The ampoule was left at 150 °C for 40 h and afterwards cooled to room temperature over 16 h. The product was washed with acetonitrile (20 mL) to remove excess pyz and residual $Mo(CO)_6$. Yield: 70 mg (70% based on Mo). Calculated (experimental) elemental analysis for $C_9H_6MoN_3O_3{\cdot}C_2H_2N$: C 38.84% (38.54%), H 2.37% (2.36%), N 16.47% (16.40%), Mo 28.21% (28.05%).

Synthesis of **W**: In three oven-dried ampoules ($V = 21$ mL) were placed $W(CO)_6$ (each: 128 mg, 0.36 mmol) and pyz (each: 480 g, 6.0 mmol). The ampoules were evacuated for 2 min to remove all oxygen and afterwards flame sealed. The ampoules were inserted into a furnace and the temperature was ramped to 200°C over the course of 4 h. The ampoules were left at 200°C for 40 h and afterwards cooled to room temperature over 16 h. The dark products were each washed with acetonitrile (20 mL) to remove excess pyz and residual $W(CO)_6$. The product of the three syntheses were combined in a separatory funnel. Under slight evolution of heat, *N*,*N*-dimethylformamide (14 mL) was stirred into bromoform (45 mL). The solvent mixture was added to the separatory funnel and the solid divided into a lower and an upper fraction of **cubicW** and **W**, respectively. After a few hours of separation, the upper fraction was removed from the separation funnel and filtered, washed with acetonitrile (10 mL) and dried *in vacuo*. Yield: 272 mg (58% based on W). Calculated (experimental) elemental analysis for $C_9H_6N_3O_3W \cdot C_2H_2N$: C 30.87% (30.51%), H 1.88% (1.85%), N 13.09% (12.89%), W 42.95% (42.51%).

To remove intercalated pyz molecules or exchange intercalated pyz molecules with more volatile solvent molecules, samples of **W** were

- subjected to vacuum at 150°C over three days,
- grinded and subjected to vacuum at 150°C over three days,
- heated in dichloromethane at 150°C in an autoclave for three days,
- heated in cyclohexane at 110°C for three days,
- sonicated in pentane, or
- sonicated in diethyl ether.

Subsequently, SCXRD (or PXRD for the ground sample) were used to investigate the content of the pores. None of the methods showed the non-destructive removal of the intercalated pyz molecules.

IR Spectroscopy

The attenuated-total-reflectance (ATR) Fourier Transform infrared (FTIR) spectra shown in Fig. 2 were collected by a Bruker VERTEX80v FTIR vacuum spectrometer employing a single-reflection germanium ATR accessory (IRIS) from PIKE Technologies Inc. The FTIR apparatus was configured with a KBr on Ge beam splitter, a liquid nitrogen cooled HgCDTe detector and a globar thermal radiation source. The collected ATR spectra of 1 cm^{-1} resolution have been corrected for residual water vapor absorption and the resulting absorption spectra have been corrected for minor baseline drifts. Subsequently, extended ATR corrections were applied to account for the wavelength-dependent penetration depth of the infrared probe beam into the solid samples.

Crystallography

Crystals were isolated from the reaction products and mounted on a loop onto a Supernova DualSource diffractometer. Experiments were conducted in a nitrogen stream at 120 K with Mo radiation. Using Olex2 [1], the structure of **Cr** was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL 2018/3 [3] refinement package using Least Squares minimization. The structures of **cubicCr**, **cubicMo** and **cubicW** were solved with the SHELXS [4] structure solution program using Direct Methods and refined with the SHELXL 2018/3 [3] refinement package using Least Squares minimization. The structure of **Mo** and **W** were solved with the olex2.solve 1.3 [5] structure solution program using Charge Flipping and refined with the SHELXL 2018/3 [3] refinement package using Least Squares minimization. The crystals of **Cr** were poorly diffracting and twinned and no acceptable structure solution could be obtained. The diffraction data of **Mo** was reduced as a twin and the structure was solved using the HKLF4 and the solution was refined using the HKLF5. The pyz molecules in **W** are all disordered over several positions. For the co-crystallized pyz molecules, a solvent mask was calculated, and 78 electrons per unit cell were found. This is consistent with the presence of 0.5($C_4H_4N_2$) per asymmetric unit which account for 84 electrons per unit cell. Powder diffraction experiments were conducted at room temperature with a Cu Kα1 (λ = 1.5406 Å) source on a Huber G679 diffractometer in transmission mode and with a quartz monochromator.

Table S1: Crystallographic information and refinement parameter.

Compound	**Cr**	**cubicCr**	**Mo**	**cubicMo**	**W**	**cubicW**
CCDC number	*Not deposited*	2063157	2063156	2063160	2063161	2063159
Empirical formula	$C_{11}H_8CrN_4O_3$	$C_9H_6CrN_3O_3$	$C_{11}H_8MoN_4O_3$	$C_9H_6MoN_3O_3$	$C_9H_6WN_3O_3$	$C_9H_6WN_3O_3$
Formula weight / g mol^{-1}	296.21	256.17	340.15	300.11	388.02	388.02
Temperature / K	120.0(1)	120.0(1)	120.0(1)	120.0(1)	120.0(1)	120.0(1)
Crystal system	triclinic	Cubic	triclinic	Cubic	monoclinic	Cubic
Space group	*P*-1	*I*-43*d*	*P*-1	*I*-43*d*	*C*/2*m*	*I*-43*d*
a / Å	6.812(2)	15.8757(8)	6.8571(8)	16.2253(5)	17.8974(7)	16.1383(2)
b / Å	9.619(3)	16.8757(8)	9.7204(11)	16.2253(5)	9.9861(5)	16.1383(2)
c / Å	10.153(3)	16.8757(8)	10.0406(10)	16.2253(5)	6.7067(3)	16.1383(2)
α / °	62.53(3)	90	64.131(10)	90	90	90
β / °	87.97(3)	90	88.185(9)	90	90.482(4)	90
γ / °	86.43(3)	90	86.345(10)	90	90	90
Volume / Å^3	589.1(3)	4001.3(5)	600.95(13)	4271.5(4)	1198.61(9)	4203.2(1)
Z	2	16	2	16	4	16
ρ_{calc} / g cm^{-3}	1.670	1.701	1.880	1.867	2.150	2.453
μ / mm^{-1}	0.980	1.137	1.101	1.222	9.632	10.987
F(000)	300.0	2064.0	336.0	2352.0	716.0	2864.0
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2θ range for data collection / °	7.472 to 54.97	7.26 to 56.422	7.358 to 52.736	7.104 to 54.158	7.562 to 54.202	7.142 to 59.382
Index ranges	$-8 \le h \le 8$	$-12 \le h \le 16$	$-8 \le h \le 8$	$-18 \le h \le 4$	$-22 \le h \le 21$	$-20 \le h \le 21$
	$-11 \le k \le 12$	$-20 \le k \le 12$	$-11 \le k \le 12$	$-20 \le k \le 13$	$-11 \le k \le 12$	$-21 \le k \le 21$
	$-13 \le l \le 12$	$-17 \le l \le 4$	$-12 \le l \le 12$	$-16 \le l \le 13$	$-8 \le l \le 6$	$-19 \le l \le 21$
Reflections collected	4834	1916	4212	2128	5042	18475
Independent reflections	2604 [R_{int} = 0.0906]	739 [R_{int} = 0.0373]	4212	727 [R_{int} = 0.0539]	1392 [R_{int} = 0.0384]	972 [R_{int} = 0.0567]
Data/restraints/parameters	2604/0/142	739/0/55	4212/0/177	727/0/49	1392/23/127	972/0/49
Goodness-of-fit on F^2	1.052	1.107	0.868	1.071	1.018	1.113
Final R_1 index [$F^2 \geq 2\sigma(F^2)$]	0.1257	0.0359	0.0361	0.0305	0.0241	0.0170
Final wR_2 index [F^2]	0.3489	0.0766	0.0672	0.0546	0.0420	0.0252
Largest diff. peak/hole / e Å^{-3}	4.11/–0.98	0.28/–0.22	0.53/–0.64	0.38/–0.32	1.29/–0.83	0.47/–0.53

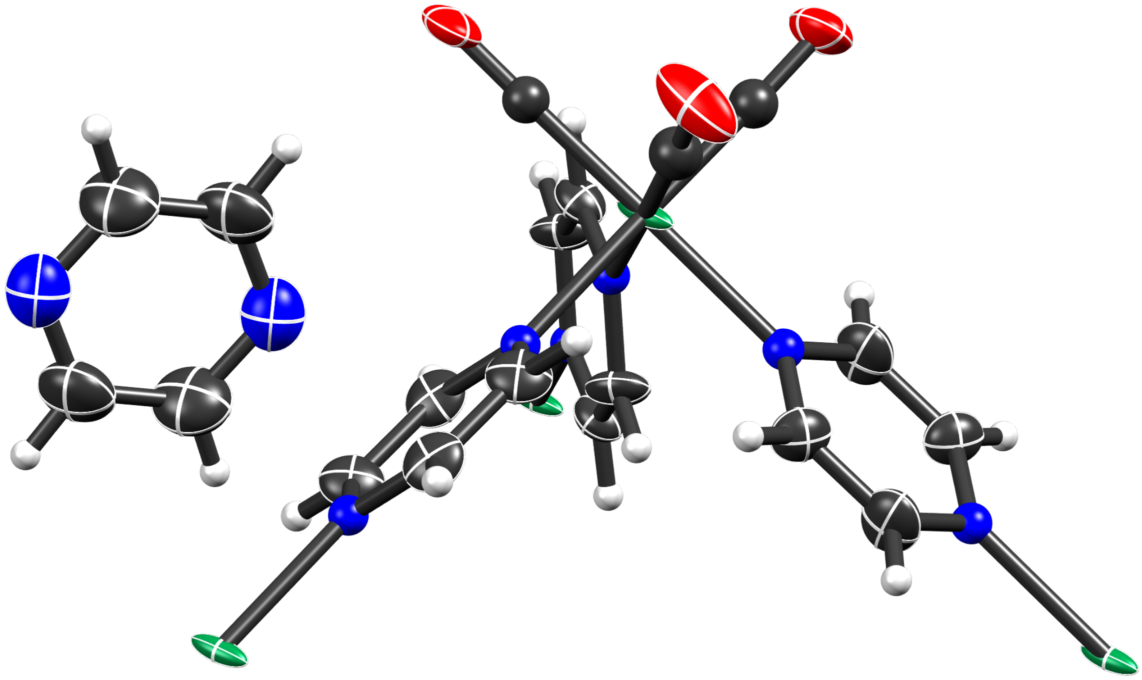

Figure S1: Thermal ellipsoid plot of the low-quality structure of **Cr** at 80% probability level. The N atom of *μ*-pyz and the C atom of (CO) were refined isotropically. Cr green, C grey, N blue, O red, H white.

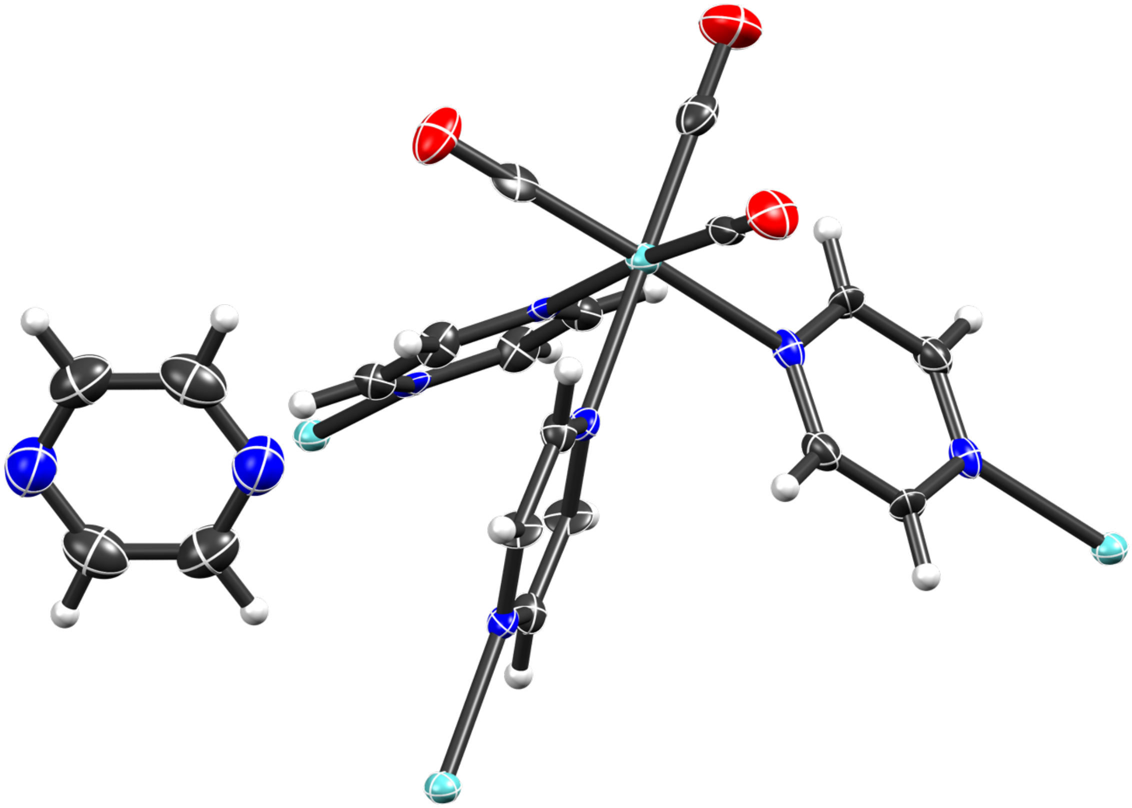

Figure S2: Thermal ellipsoid plot of **Mo** at 80% probability level. Mo turquoise, C grey, H white, N blue, O red.

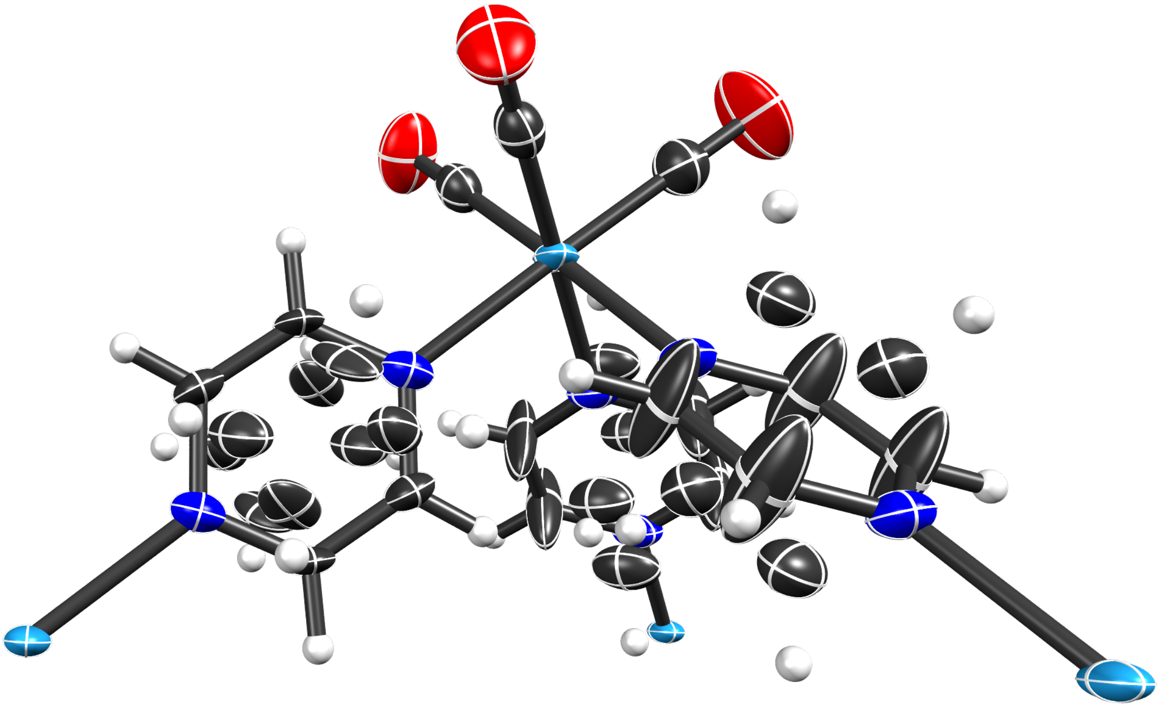

Figure S3: Thermal ellipsoid plot of **W** at 80% probability level. The co-crystallized pyz molecule is calculated with a solvent mask and not shown. Some of the C atoms of *μ*-pyz were refined isotropically. W light blue, C grey, N blue, O red, H white.

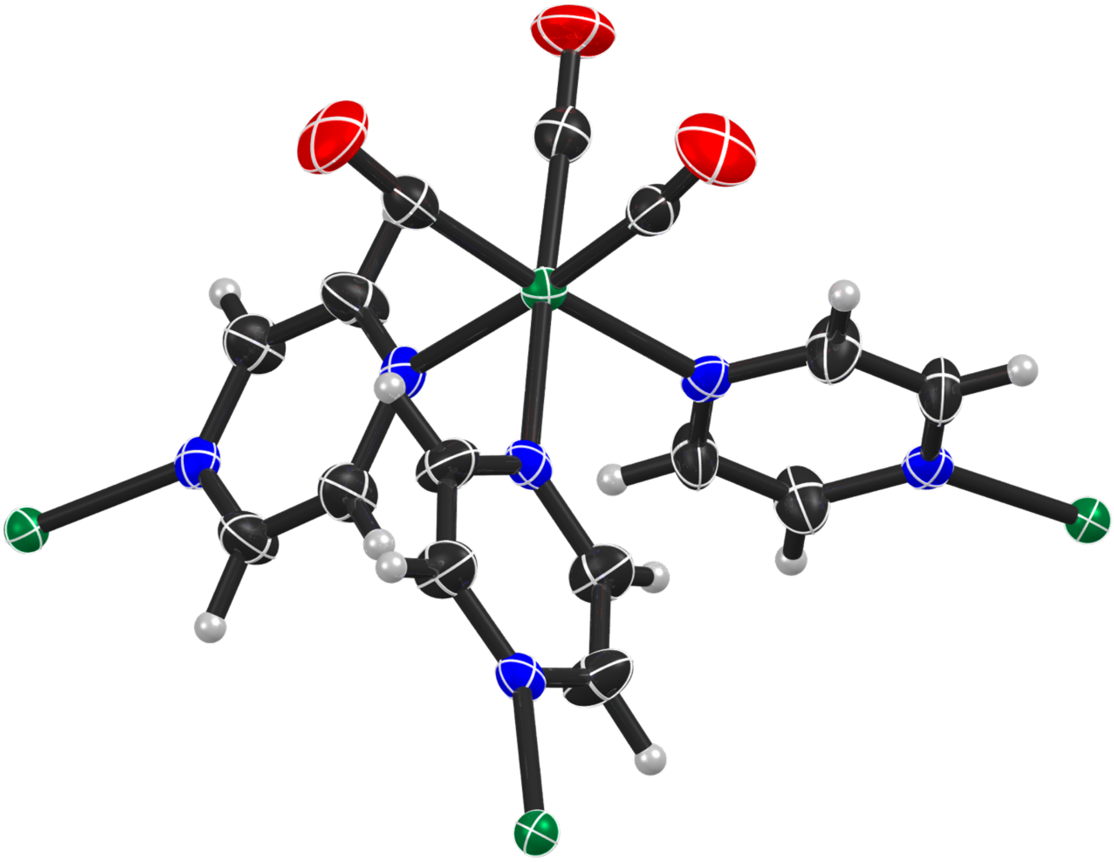

Figure S4: Thermal ellipsoid plot of **cubicCr** at 80% probability level. Cr green, C grey, N blue, O red, H white.

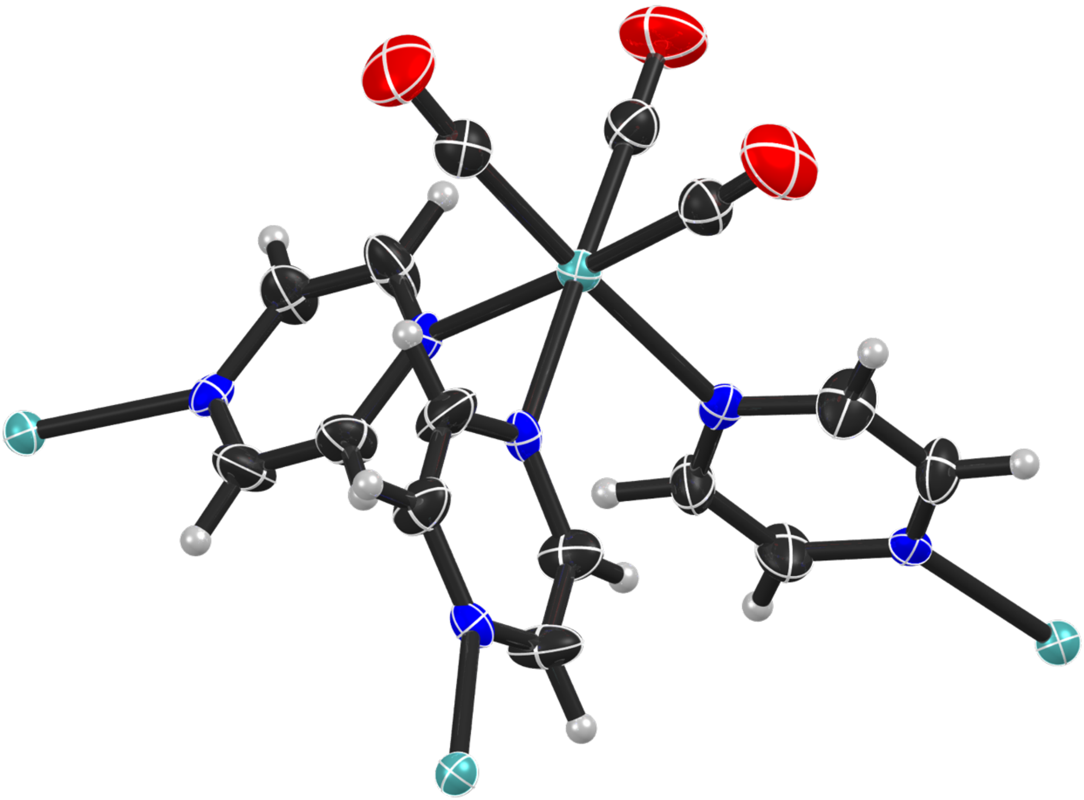

Figure S5: Thermal ellipsoid plot of **cubicMo** at 80% probability level. Mo turquoise, C grey, N blue, O red, H white.

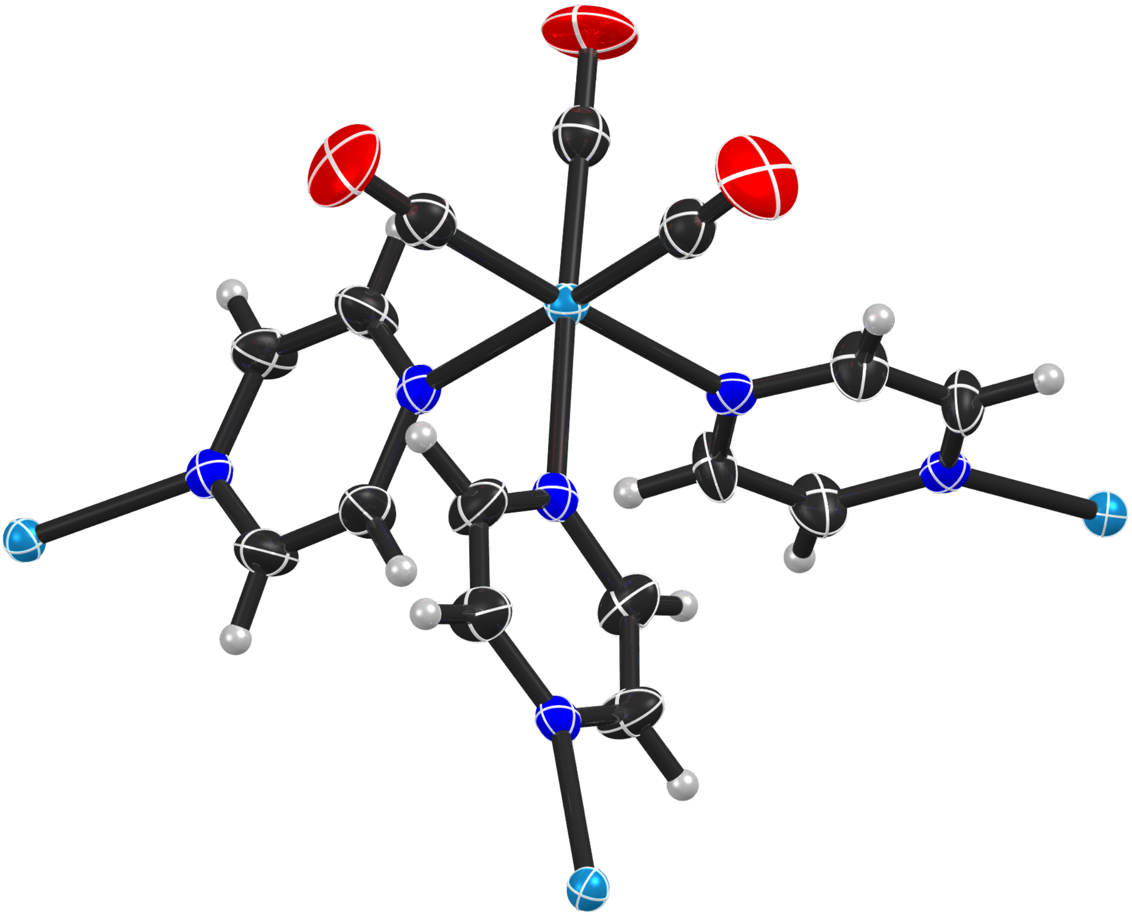

Figure S6: Thermal ellipsoid plot of **cubicW** at 80% probability level. W light blue, C grey, N blue, O red, H white.

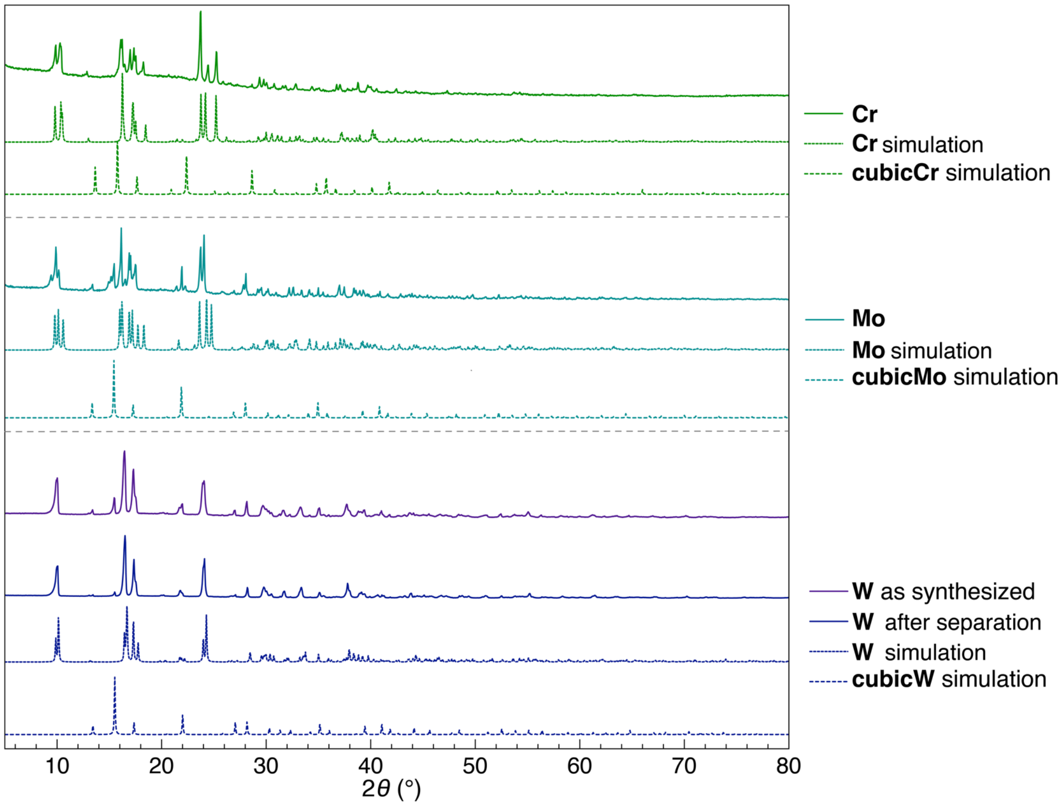

Figure S7: Experimental (RT) and simulated (120 K) powder X-ray diffractograms. For **W** spectra from before and after the separation from **cubicW** are shown.

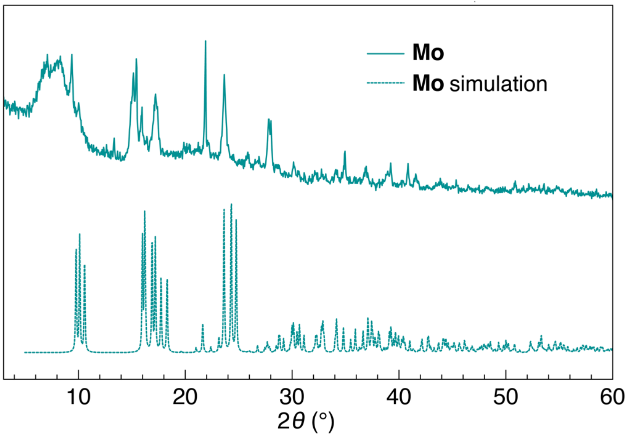

Figure S8: Experimental (RT) and simulated (120 K) PXRD spectra of one polycrystalline sample of **Mo** after one year of air exposure.

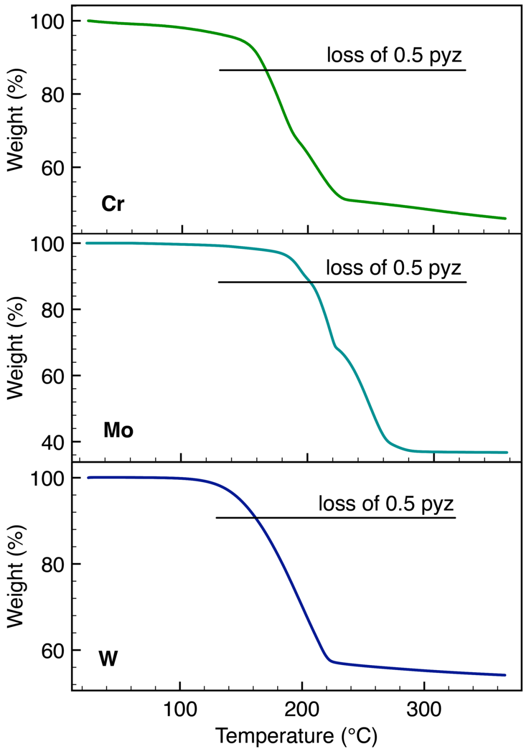

Figure S9: Thermogravimetric analysis of **Cr**, **Mo**, **W** measured at 1 K min^{-1}.

References

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst*. **42**, 339-341.

[2] Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8.

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[4] Sheldrick, G.M. (2008). *Acta Cryst.* **A64**, 112-122.

[5] Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). *Acta Cryst.* **A71**, 59-75.