Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Synthesis and Reactivity of Coordinatively Unsaturated Halocarbonyl Molybdenum PNP Pincer Complexes

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Table S1. Crystal structure determination of second polymorph of compound **4**, [Mo(PNP^{Me}-*i*Pr)(CO)-Br$_2$]**.** The first polymorph is designated as **4**, the second polymorph as **4b**, and for comparison the crystallographic data of both polymorphs are given here.

Compound code	**4** (4-1680)	**4b** (4b-1702)
formula	$C_{20}H_{37}Br_2MoN_3OP_2$	$C_{20}H_{37}Br_2MoN_3OP_2$
fw	653.23	653.23
cryst.size, mm	0.28 x 0.25 x 0.23	0.28 x 0.25 x 0.23
color, shape	green block	green plate
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a, Å	15.3996(8)	19.1328(5)
b, Å	11.2076(5)	8.9912(2)
c, Å	15.6189(7)	29.1561(7)
α, deg	90	90
β, deg	105.005(2)	92.475(2)
γ, deg	90	90
V, Å^3	2603.8(2)	5011.0(2)
T, K	100(2)	100(2)
Z	4	8, Z' = 2
ρ_{calc}, g cm^{-3}	1.666	1.732
μ, mm^{-1} (MoKα)	3.712	3.858
F(000)	1312	2624
absorption corrections	multi-scan, 0.44–0.36	multi-scan, 0.62–0.86
θ range, deg	2.16–30.00	1.72–30.00
no. of rflns measd	54727	127063
R_{int}	0.023	0.046
no. of rflns unique	7581	14602
no. of rflns $I>2\sigma(I)$	7003	12024
no. of params / restraints	272 / 0	543 / 0
R_1 ($I > 2\sigma(I)$) [a]	0.0195	0.0342
R_1 (all data)	0.0229	0.0478
wR_2 ($I > 2\sigma(I)$)	0.0483	0.0625
wR_2 (all data)	0.0498	0.0663
Diff.Four.peaks min/max, eÅ^{-3}	-0.38 / 1.15	-1.64 / 1.09

[a] $R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$, $\mathrm{GooF} = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$

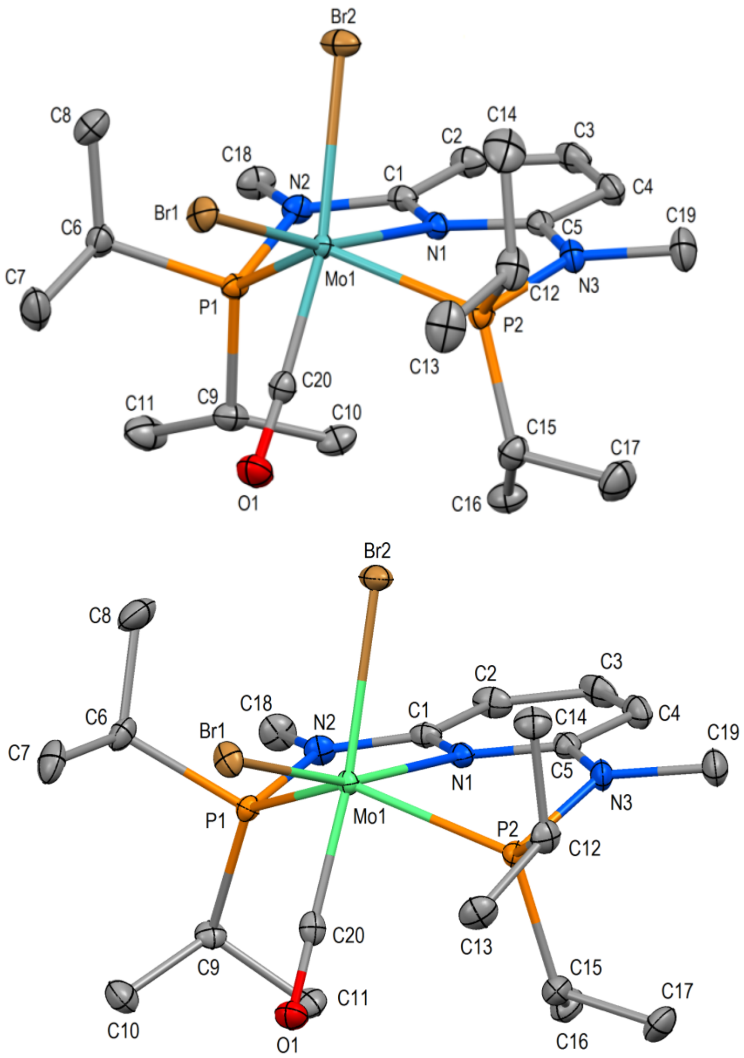

Fig. S1. Comparison of the [Mo(PNP^{Me}-*i*Pr)(CO)Br$_2$] complexes in the two polymorphs **4** (top) and **4b** (bottom). 50% displacement ellipsoids and H atoms omitted for clarity. Bond distances and bond angles of the two complexes agree typically within better than 0.02 Å and 2°. The difference between the two molecular structures concerns the orientation of the isopropyl group C9-C10-C11 which exhibits a torsion angle Mo1-P1-C9-H9 of 42.3° in **4** and 166.6° in **4b** (H9 is the C9 bonded *i*Pr hydrogen atom that is not shown in the figures; H9 points toward O1 in **4**, and away from O1 in **4b**). The remaining *i*Pr groups have basically the identical orientations in both complexes. The crystal lattices of both polymorphs are different.

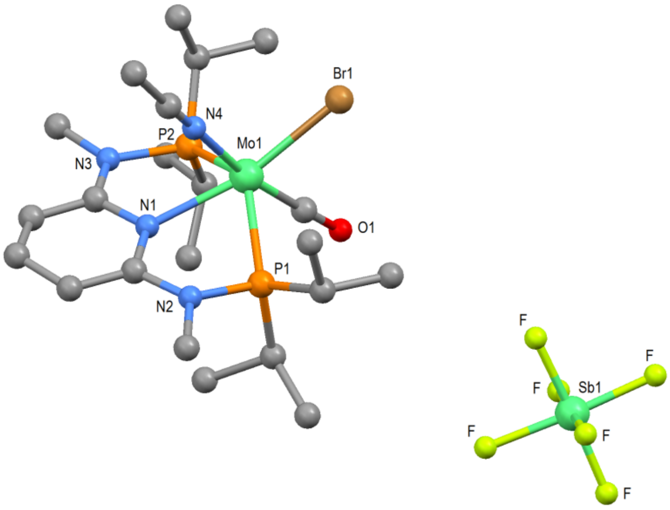

Fig. S3. X-ray crystal structure model of [Mo(PNP$^{\mathrm{Me}}$-*i*Pr)(CO)(CH$_3$CN)Br]SbF$_6$ **(6)** in ball-and-stick representation (H atoms omitted for clarity) obtained from a very poor reflection data set collected at T = 100 K. The structure refinement ended with an unsatisfactory R1 = 0.165 for 6866 independent reflections but was able to proof that the acetonitrile ligand is trans to the carbonyl group, in accordance with other experimental evidence (see text). The very poor diffraction data were due to the large content of destabilizing disordered solvent in the crystal lattice that is located in channels along the c-axis of the tetragonal unit cell (s.g. P4/n, a = 28.74(3) Å, c = 8.692(11) Å, V = 7177(13) Å^3, Z = 8). Due to the insufficient quality of the crystal structure, a CIF was not deposited but is available upon request from the authors.

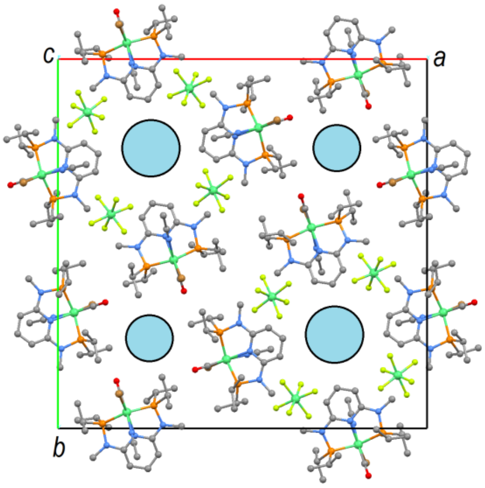

Fig. S4. X-ray crystal structure model of [Mo(PNP$^{\mathrm{Me}}$-*i*Pr)(CO)(CH$_3$CN)Br]SbF$_6$ **(6)** showing a projection along the c-axis (tetragonal, s.g. P4/n, a = 28.74(3) Å, c = 8.692(11) Å, V = 7177(13) Å^3, Z = 8) with the channels containing destabilizing disordered solvent (acetonitrile/pentane) as blue circles. The total potential solvent accessible void volume is ca. 1000 Å^3 per unit cell (program PLATON; Spek, A. L. (2009). *Acta Cryst.* D**65**, 148-155).