Supporting information of the manuscript entitled:

The reaction behavior of $[Cp_2Mo_2(CO)_4(\mu,\eta^{2:2}-P_2)]$ and $[Cp''Ta(CO)_2(\eta^4-P_4)]$ towards hydroxide and *tert*-Butyl nucleophiles

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Experimental details: complex syntheses and characterization Experimental and simulated NMR spectra Details on X-ray structure determinations References

General procedures: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line in Argon atmosphere or in Argon filled glove box with a high-capacity recirculator (<0.1 ppm O₂). Toluene thf, dme and *n*-hexane were dried using conventional techniques, degassed and saturated with Argon. Deuterated solvents were degassed, dried and distilled prior to use. The complexes $[Cp_2Mo_2(CO)_4(\mu,\eta^{2:2}-P_2)]^{[1]}$ (1) and $[Cp''Ta(CO)_2(\eta^4-P_4)]^{[2]}$ (2) and the NHC IDipp^[3] were prepared according to its published procedure. NMR spectra were recorded on a Bruker Avance 300 MHz and Bruker Avance 400 MHz spectrometers. Chemical shifts are given in ppm; they are referenced to TMS for ¹H and ¹³C, and 85% H₃PO₄ for ³¹P as external standard. Elemental analyses (CHN) were determined using in-house facility.

Experimental details: complex syntheses and characterization

Synthesis of $[K(thf)_{1.5}][3]$, $[3] = [Cp_2Mo_2(CO)_4(\mu-PH_2)]$: 100 mg (0.20 mmol) $[Cp_2Mo_2(CO)_4(\mu,\eta^{2:2}-P_2)]$ (1) and 40 mg (0.71 mmol) KOH are dissolved in 20 mL thf and stirred for seven days at 60 °C. The color of the solution is changing from orange to bordeaux. The solution was reduced to 3 mL, layered with *n*-hexane and crystalized at 4 °C. After five days clear dark plates of $[K(thf)_{1.5}][Mo_2Cp_2(CO)_4(\mu-PH_2)]$ (130 mg, 0.163 mmol, 81% yield) can be isolated.

¹**H NMR** (thf-d₈, 300 K): δ [ppm] = 4.44 (d, 2H, ¹*J*_{PH} = 318 Hz, PH₂), 4.83 (s, 10H, C₅H₅).

¹**H**{³¹**P**} **NMR** (thf-d₈, 300 K): δ [ppm] = 4.44 (s, 2H, PH₂), 4.83 (s, 10H, C₅H₅).

³¹**P**{¹**H**} **NMR** (thf-d₈, 300 K): δ [ppm] = 49.8 (s, 1P).

³¹**P NMR** (thf-d₈, 300 K): δ [ppm] = 49.8 (t, ¹*J*_{PH} = 318 Hz, 1P).

ESI-MS (dme): m/z = 466.8 (100%, $[Cp_2Mo_2(CO)_4(\mu-PH_2)]^{-}$).

EA calculated for C₁₄H₁₂KMo₂O₄P (506,19 g·mol⁻¹): C: 33.22, H: 2.39; found [%]: C: 33.74, H: 2.71.

Synthesis of $[\text{Li}(\text{dme})_3][4]$, $[4] = [\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^{2:1}\text{-}\text{PP}^t\text{Bu})]^-$: 80 mg (0.16 mmol) [Cp₂Mo₂(CO)₄($\mu, \eta^{2:2}\text{-}\text{P}_2$)] (1) are dissolved in 15 mL thf, cooled to -80°C and 21 mg (0.32 mmol, 0.19 mL) ^tBuLi in *n*-pentane is added. An instant color change from orange to brown is observed. After the solution was heated to ambient temperature overnight, all volatiles are removed, the oily residue is dissolved in 3 mL dme and layered with 9 mL *n*-hexane. Red brownish crystal blocks of [Li(dme)₃][Mo₂Cp₂(CO)₄($\mu, \eta^{2:1}$ -PP^tBu)] (50 mg, 0.060 mmol, 38% yield) are obtained after storage for five days at 4 °C.

¹**H** NMR (thf-d₈, 300 K): δ [ppm] = 0.81 (d, 9H, ^tBu), 4.58 (s, 5H, C₅H₅), 4.85 (s, 5H, C₅H₅).

³¹**P**{¹**H**} **NMR** (thf-d₈, 300 K): δ [ppm] = 191.9 (d, ¹*J*_{PP} = 454 Hz, *P*-P-^tBu), 59.8 (d, ¹*J*_{PP} = 454 Hz, P-*P*-^tBu).

³¹**P NMR** (thf-d₈, 300 K): δ [ppm] = 191.9 (d, ¹*J*_{PP} = 454 Hz, *P*-P-^tBu), 59.8 (m, ¹*J*_{PP} = 454 Hz, P-*P*-^tBu). The exact ³*J*_{PH} coupling constant could not be determined.

ESI-MS (dme) $m/z = 552.9 (100\%, [Cp_2Mo_2(CO)_4(\mu, \eta^{2:1}-PP^tBu)]^{-}).$

EA calculated for $C_{27.2}H_{37.4}LiMo_2O_{6.3}P_2$ (725.95 g·mol⁻¹): C: 45.00, H: 5.19; found [%]: C: 44.70, H: 5.19.

Synthesis of [IDipp-H][5], [5] = [Cp''Ta(CO)₂(η^3 -P₄(O)H)][:] 80 mg (0.15 mmol) of [Cp''Ta(CO)₂(η^4 -P₄)] (2) were dissolved and 5 mL of a stock solution of H₂O in thf (c = 0.029 mmol·mL⁻¹) were added. No color change was observed. Afterwards, 58 mg (0.15 mmol) of IDipp were dissolved in thf and added to the sunny yellow solution of 1 and H₂O. A light color change to light brown was observed and the solution was stirred for three days, were the brown coloring of the solution got intensified. After removing all volatiles in vaccuo, the brown residue was dissolved in 3 mL dme, was layered by 15 mL *n*-hexane and stored at 4°C to obtain brown blocks of [IDipp-H][Cp''Ta(CO)₂(η^3 -P₄OH)] (114 mg, 0.12 mmol, 81% yield).

¹**H NMR** (thf-d₈, 300 K): δ [ppm] = 1.28 (s, 18H, Cp², 'Bu), 1.32 (d, 12H, Dipp ⁱPr, ³*J*_{HH} = 6.8 Hz), 1.36 (d, 12H, Dipp ⁱPr, ³*J*_{HH} = 6.8 Hz), 2.65 (sept, 4H, Dipp ⁱPr, ³*J*_{HH} = 6.8 Hz), 5.35 (d, 2H, CH, ⁴*J*_{HH} = 2.0 Hz), 5.59 (t, 1H, CH, ⁴*J*_{HH} = 2.0 Hz), 6.40 (dtd, 1H, H-P, ¹*J*_{PH} = 362.3 Hz, ²*J*_{PH} = 21.2 Hz, ³*J*_{PH} = 4.3 Hz), 8.41 (s, 2H, H-CN), 11.64 (s, 1H, N2C-H).

³¹**P**{¹**H**} **NMR** (thf-d₈, 300 K): δ [ppm] = 60.1 (t, 1P, P_A), 40.2 (t, 2P, P_{M,M'}), -114.8 (t, 1P, P_x).

For coupling constants see Table S 1.

³¹**P NMR** (thf-d₈, 300 K): δ [ppm] = 60.1 (m, 1P, P_A), 40.2 (td, 2P, P_{M,M'}), -114.8 (t, 1P, P_x). For coupling constants see Table S 2.

ESI-MS (dme): anion mode: $m/z = 555.00 (100 \%, [M]^{-})$, cation mode: $m/z = 389.29 (100\%, [(IDipp-H]^{+}))$.

EA: due to the high sensitivity of [IDipp-H][Cp''Ta(CO)₂(η^3 -P₄OH)] towards moisture and air, it was not possible to obtain an exact elemental analysis. Although several samples were used.

Synthesis of [Li(thf)₄][6], [6] = [Cp"Ta(CO)₂(η^3 -P₄'Bu)][:] A solution of 100 mg (0.18 mmol) [Cp"Ta(CO)₂(η^4 -P₄)] (2) in 20 mL thf is cooled down to -80 °C and 0.16 mL (0.18 mmol) 'BuLi in *n*-pentane was added. An instant color change from sunny yellow to red is obtained. The reaction mixture is warmed up to ambient room temperature overnight. The solution was reduced to 3 mL and layered with 10 mL n-hexane. Clear light brown plates of [Li(thf)₄][Cp"Ta(CO)₂(η^3 -P₄'Bu)] (85 mg, 0.096 mmol, 53%) are formed after 4 days at 4°C.

¹**H NMR** (thf/C₆D₆ capillary, 300 K): δ [ppm] = 1.61 (s, 18H, Cp^{''} ¹Bu), 1.77 (d, 9H, P-^tBu), 6.03 (t, 1H, CH, ⁴J_{HH} = 2.0 Hz), 6.16 (d, 2H, CH, ⁴J_{HH} = 2.0 Hz).

³¹P{¹H} NMR (thf/C₆D₆ capillary, 300 K): δ [ppm] = 108.1 (dt, P_A), -15.1 (dt, P_M), -89.8 (dd, P_{X,X}). For coupling constants see Table S 3.

³¹**P** NMR (thf/C₆D₆ capillary, 300 K): δ [ppm] = 108.1 (m, P_A), -15.1 (dt, P_M), -89.8 (dd, P_{X,X}), the phosphorus phosphorus coupling are the same like in the ³¹P{¹H} NMR spectrum. The exact ³J_{PH} coupling constant could not be determined.

ESI-MS (dme): m/z = 1197.4 (100%, {[Cp''Ta(CO)₂(η^3 -P₄-^tBu)]₂+[Li⁺]}⁻).

EA calculated for C₁₉H₃₀O₂P₄TaLi (602,22 g·mol⁻¹): C: 37.89, H: 5.02; found [%]: C: 37.69, H: 4.95.

Experimental and simulated NMR spectra



Figure S 1. ³¹P NMR spectrum (top) and ³¹P{¹H} NMR spectrum (bottom) of compound **3** at 300 K in thf-d₈.



Figure S 2. ${}^{1}H{}^{31}P{}$ NMR spectrum (top) and ${}^{1}H$ NMR spectrum (bottom) from 4.9 to 4.0 ppm of **3** at 300 K in thf-d₈.



Figure S 3. ³¹P NMR spectrum (top) and ³¹P{¹H} NMR spectrum (bottom) of 4 at 300 K in thf-d₈.



Figure S 4. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR spectrum of 5 at 300 K in thf-d₈.

Table S 1. ${}^{31}P{}^{1}H$ NMR chemical shifts and coupling constants for **5** obtained from the simulation.

J (Hz)				δ (ppm)	
$^1 J_{\mathrm{P}_\mathrm{A},\mathrm{P}_\mathrm{M}}$	230.2	$^{1}J_{\mathrm{P}_{\mathrm{M}},\mathrm{P}_{\mathrm{X}}}$	232.4	PA	60.1
$^{1}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{M}^{\circ}}}$	233.2	$^{1}J_{\mathrm{P}_{\mathrm{M}^{\circ},\mathrm{P}_{\mathrm{X}}}}$	226.3	$P_M, P_{M'}$	40.2
$^2 J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}}$	7.5	$^{2}J_{\mathrm{P}_{\mathrm{M}},\mathrm{P}_{\mathrm{M}^{\circ}}}$	0.5	P _X	-114.8



Figure S 5. Experimental (top) and simulated (bottom) ³¹P NMR spectrum of 5 at 300 K in thf-d₈.

 Table S 2. ³¹P NMR chemical shifts and coupling constants for 5 obtained from the simulation.

J (Hz)				δ (ppm)	
$^{1}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{M}}}$	232.2	$^{1}J_{\mathrm{P_{M},P_{X}}}$	231.6	PA	60.1
$^{1}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{M}^{\circ}}}$	232.2	$^{1}J_{\mathrm{P}_{\mathrm{M}^{\circ},\mathrm{P}_{\mathrm{X}}}}$	230.1	$P_M, P_{M'}$	40.2
$^{2}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}}$	3.5	$^{2}J_{\mathrm{P}_{\mathrm{M}},\mathrm{P}_{\mathrm{M}^{\circ}}}$	-4.0	P _X	-114.8
$^{1}J_{\mathrm{P}_{\mathrm{A}},\mathrm{H}}$	362.3	$^{2}J_{\mathrm{P}_{\mathrm{M}^{\circ},\mathrm{H}}}$	21.4		
$^{2}J_{\mathrm{P}_{\mathrm{M}},\mathrm{H}}$	21.0	$^{3}J_{\mathrm{P}_{\mathrm{X}},\mathrm{H}}$	4.3		



Figure S 6. Experimental (top) and simulated (bottom) ${}^{31}P{}^{1}H$ NMR spectrum of **6** at 300 K in thf with a C₆D₆ capillary. Impurities are marked with *.

Table S 3. ³¹P NMR chemical shifts and coupling constants for 6 obtained from the simulation.

J (Hz)		δ (ppm)		
$^{2}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{M}}}$	16.8	PA	108.1	
$^{1}J_{\mathrm{P}_{\mathrm{M}},\mathrm{P}_{\mathrm{X}}}$	150.8	P _M	-15.1	
$^{1}J_{\mathrm{P}_{\mathrm{A}},\mathrm{P}_{\mathrm{X}}}$	232.9	P _X	-89.8	

Details of the X-ray structure determinations

All single crystal structure analyses were performed using a Rigaku GV50 diffractometer equipped with a TitanS2 detector. Frames integration and data reduction were performed with the CrysAlisPro (Version 1.171.37.34 ([K(thf)_{1.5}][**3**]), 1.171.41.54a ([IDipp-H][**5**], [Li(thf)₄][**6**])^[4] software package. For the compounds [K(thf)_{1.5}][**3**] and [IDipp-H][**5**] a numerical absorption correction based on a gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics, as implemented in SCALE3 ABSPACK scaling algorithm was applied. For compound [Li(thf)₄][**6**] a multi-scan absorption correction using spherical harmonics, as implemented in SCALE3 ABSPACK scaling algorithm was used. Using Olex2,^[5] all structures were solved by ShelXT^[6] ([IDipp-H][**5**], [Li(thf)₄][**6**]) or SIR97^[7] ([K(thf)_{1.5}][**3**]) and a least-square refinement on F2 was carried out with ShelXL.^[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. The figures were created with Olex2.^[5]

Compound $[K(thf)_{1.5}][3]$: The asymmetric unit contains three molecules of $[Cp_2Mo_2(CO)_4(\mu-PH_2)]^-$, three K⁺ cations and 4.5 thf solvent molecules. One K atom and the four coordinating thf molecules as well as one coordinating CO ligand are disordered over two positions (56:44). Further, a Cp ligand and one CO ligand of a $[Cp_2Mo_2(CO)_4(\mu-PH_2)]^-$ unit is disordered over two positions (56:44). To describe these disorders the DFIX, SADI, DANG, ISOR, RIGU and SIMU restraints were applied. Additionally compound $[K(thf)_{1.5}][3]$ was refined as a 2-component inversion twin.

Compound [IDipp-H][**5**]: The asymmetric unit contains one molecule of $[Cp''Ta(CO)_2(\eta^3-P_4(O)H)]^{-1}$ and one IDipp-H molecule. The Cp'' ligand is disordered over two position (79:21). Additionally is the Ta atom (59:41) and an *i*Pr group (67:33) of the IDipp-H unit disordered over two position. To describe these disorders the SADI and SIMU restraints were applied.

Compound [Li(thf)₄][**6**]: The asymmetric unit contains one molecule of $[Cp''Ta(CO)_2(\eta^3-P_4'Bu)]^-$ and a Li cation coordinated by four thf molecules. Two of the four thf molecules are disordered over two positions (52:48; 57:43). To describe these disorders the SADI and SIMU restraints were applied.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for **3**, **5** and **6** are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-2026418 (**3**), CCDC-2026419 (**5**) and CCDC-2026420 (**6**), respectively. These data can be obtained free of charge at 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).

All crystals of compound $[Li(dme)_3][4]$ were twinned and the overall crystal quality was poor, although several recrystallization attempts were performed. Further, the crystals show fast decomposition after they are removed from the mother liquor (even at low temperatures). However, it was possible to measure a crystal of compound $[Li(dme)_3][4]$, which allowed us to determine the connectivity unambiguously. The crystallographic data of $[Li(dme)_3][4]$ are given below.

Crystallographic Data of [Li(dme)₃][**4**]: C₃₀H₄₉LiMo₂O₁₀P₂, $M_r = 830.45$, monoclinic, P_{21}/n (No. 14), a = 15.1611(6) Å, b = 13.8952(4) Å, c = 18.8307(7) Å, $\beta = 111.936(4)^{\circ}$, $\alpha = \gamma = 90^{\circ}$, V = 3679.8(2) Å³, T = 141.51(10) K, Z = 4, Z' = 1, μ (Cu K_{α}) = 6.819, 11972 reflections measured, 11972 unique (R_{int} = 0.1017.) which were used in all calculations. The wR_2 was 0.3807 (all data) and R_1 was 0.1197 (I ≥ 2 *s*(I)).

Compound	[K(thf) _{1.5}][3]	[IDipp-H][5]	[Li(thf) ₄][6]
Data set	FR033	FR110	FR073
(Internal naming) CCDC	2026418	2026419	2026420
Formula	$C_{60}H_{72}K_2M_{06}O_{16}$	$C_{46}H_{60}N_2O_4P_4T_3$	C25H61LiO6P4Ta
$D_{calc} / g \cdot cm^{-3}$	1 768	1 366	1 426
m/mm^{-1}	11 430	5 631	6 664
Formula Weight	1843.02	1018.86	889.60
Colour	clear dark red	brown	clear light brown
Shape	plate	block	plate
Size/mm ³	0.41×0.39×0.08	0.18×0.07×0.05	0.61×0.35×0.06
T/K	122.99(13)	122.99(19)	123.00(10)
Crystal System	monoclinic	orthorhombic	monoclinic
Space Group	<i>C</i> 2	Pbca	$P2_{1}/n$
a/Å	43.5147(8)	19.8677(4)	11.86250(10)
b/Å	7.94643(15)	17.9409(3)	21.7618(3)
c/Å	20.3986(3)	27.8048(6)	16.0909(2)
$\alpha/^{\circ}$	90	90	90
β/°	100.9442(15)	90	94.0170(10)
$\gamma/^{\circ}$	90	90	90
$V/Å^3$	6925.3(2)	9910.9(3)	4143.65(8)
Ζ	4	8	4
Ζ'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	CuK_{α}	Cu K _a	Cu K _a
$Q_{min}/^{\circ}$	2.723	3.179	3.421
$Q_{max}/^{\circ}$	74.437	74.366	74.316
Measured Refl.	53433	50470	27131
Independent Refl.	12674	9939	8180
Reflections with $I > 2(I)$	11748	8929	7348
R _{int}	0.0796	0.0528	0.1071
Parameters	1116	631	488
Restraints	562	220	148
Largest Peak	1.066	1.476	2.009
Deepest Hole	-0.901	-1.204	-2.103
GooF	1.046	1.176	1.031
wR_2 (all data)	0.1196	0.1519	0.1366
wR_2	0.1144	0.1496	0.1318
R_1 (all data)	0.0515	0.0825	0.0542
R_1	0.0452	0.0772	0.0503

 Table S 4: Crystallographic data and detail of the compounds 3, 5 and 6.



Figure S 7. Section of the molecular structure of [K(thf)_{1.5}][**3**] in the solid state. All thf molecules are drawn in the balls and sticks model. H atoms are omitted for clarity. Selected distances [Å] and angles [°]: Mo1-P1 2.375(2), Mo2-P1 2.378(2), Mo1-Mo2 3.1826(10), P1-Mo1-Mo2 48.00(6), P1-Mo2-Mo1 47.93(6), Mo1-P1-Mo2 84.07(8).



Figure S 8. Molecular structure of [Li(dme)₃][**4**] in the solid state. H atoms are omitted for clarity. No distances or angles given, because of the unsatisfying result of the X-ray experiments. Picture is shown to verify the certain atom connectivity.



Figure S 9. Molecular structure of [IDipp-H][**5**] in the solid state. The Dipp ligands are drawn in the balls and sticks model. Except the phosphorus bonded H atom and the Carbene C bonded H atom, are all H atoms omitted for clarity. Selected distances [Å] and angles [°]: Ta1B-P2 2.447(7), Ta1B-P3 2.514(3), Ta1B-P4 2.541(5), P1-P2 2.171(3), P2-P3 2.208(3), P3-P4 2.208(3), P4-P1 2.169(3), P1-O3 1.511(7), P1-P2-P3 84.21(13), P2-P3-P4 88.11(11), P3-P4-P1 84.23(12), P4-P1-P2 90.07(12).



Figure S 10. Molecular structure of [Li(thf)₄][**6**] in the solid state. H atoms are omitted for clarity. The Cp'' ligand, the Li atom and all thf molecules are drawn in balls and sticks model. Selected distances [Å] and angles [°]: Ta1-P2 2.6046(10), Ta1-P3 2.5778(9), Ta1-P4 2.5971(10), P1-P2 2.2047(14), P2-P3 2.2074(14), P3-P4 2.2005(14), P4-P1 2.2167(14), P1-C16 1.903(4), P1-P2-P3 91.63(5), P2-P3-P4 84.02(5), P3-P4-P1 91.50(5), P4-P1-P2 83.70(5).

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