

Hydrogen-bonded adducts between neutral molecules and $[\text{Mo}(\eta^3\text{-methallyl})(\text{CO})_2(\text{HOC}(\text{py})_3)]^+$: snapshots of a deprotonation.

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Experimental Section: All manipulations were carried out at room temperature under a dinitrogen atmosphere employing Schlenk techniques. CH_2Cl_2 was dried over CaH_2 , THF and diethylether over Na-benzophenone, and hexane over sodium. IR and NMR spectra were recorded on Perkin Elmer FT1720-X and Bruker AV-400, AV-300 spectrometers respectively. Deuterated solvents were degassed by three freeze-pump-thaw cycles, dried over 4\AA molecular sieves and stored in the dark. $[\text{MoCl}(\eta^3\text{-methallyl})(\text{CO})_2(\text{NCMe})_2]$,¹ NaBAR'_4 ,² $\text{HOC}(\text{py})_3$,³ and $\text{HOC}(\text{Ph})(\text{py})_2$ ⁴ were prepared according to literature procedures. All other chemicals were purchased and used without further purification.

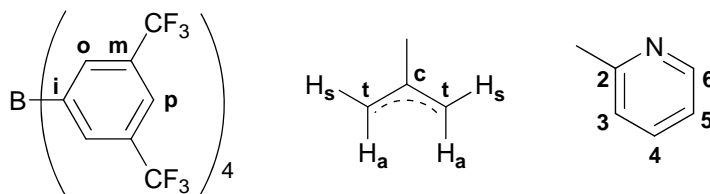


Figure 1S: Labeling scheme for BAR'_4 , methallyl and 2-pyridyl.

$\text{Mo}(\eta^3\text{-methallyl})(\text{CO})_2(\text{HOC}(\text{py})_3)[\text{BAR}'_4]$ (1H). A mixture of $[\text{MoCl}(\eta^3\text{-methallyl})(\text{CO})_2(\text{NCMe})_2]$ (0.100 g, 0.308 mmol), $\text{HOC}(\text{py})_3$ (0.081 g, 0.308 mmol) and NaBAR'_4 (0.273 g, 0.308 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 hour and filtered through diatomaceous earth. After *in vacuo* concentration to ca. 5 mL, the orange solution was layered with hexane (10 mL) and placed at $-20\text{ }^\circ\text{C}$ for two days, yielding red crystals, one of which was used for an X-ray structure determination. Yield: 0.350g, 85%. Anal. Calcd. for $\text{C}_{54}\text{H}_{32}\text{BF}_{24}\text{MoN}_3\text{O}_3$: C, 48.64; H, 2.42; N, 3.15. Found: C, 48.45; H, 2.40; N, 3.35. IR (CH_2Cl_2) ν_{CO} (cm^{-1}): 1956 vs, 1869 s; (KBr) ν_{CO} (cm^{-1}): 1963 f, 1870 f. ^1H RMN(CD_2Cl_2): 11.16 [s_{br}, 1H, O-H], 9.42 [s, 2H, H_6 py_{coord}], 8.77 [d (4.8), 1H, H_6 py_{unc}], 8.28 [t (7.8), 1H, H_4 py_{unc}], 8.12 [d (7.8), 1H, H_3 py_{unc}], 7.89 [t (7.8), 2H, H_4 py_{coord}], 7.82 [s, 8 H_o of BAR'_4], 7.73 [m, 3H, H_{py}], 7.62 [s, 4H, H_p of BAR'_4], 7.55 [t (6.1), 2H, H_5 py_{coord}], 3.48 [s, 2H, H_{syn}], 1.68 [s, 2H, H_{anti}], 1.44 [s, 3H, CH_3 of methallyl]. $^{13}\text{C}\{^1\text{H}\}$

NMR(CD₂Cl₂): 227.7 [s, CO], 161.8 [c (J(C,B)= 49.8), C_i of BAr'₄], 155.2 [s, py], 154.8 [s, py], 148.4 [s, py], 147.3 [s, py], 141.2 [s, py], 140.2 [s, py], 134.8 [s, C_o of BAr'₄], 129.2 [m, C_m of BAr'₄], 126.5 [s, py], 125.6 [s, py], 124.7 [c (J(C,F)= 272.3), CF₃ of BAr'₄], 124.3 [s, py], 121.1 [s, py], 117.5 [s, C_p of BAr'₄], 85.6 [s, C-OH], 83.5 [s, C_c of methallyl], 57.2 [s, C_t of methallyl], 19.1 [s, CH₃ of methallyl].

[Mo(η³-methallyl)(CO)₂(HOC(py)₃)](OTf) (1H(OTf)). A mixture of [MoCl(η³-methallyl)(CO)₂(NCMe)₂] (0.050 g, 0.154 mmol), HOC(py)₃ (0.045 g, 0.154 mmol) and AgOTf (0.047 g, 0.183 mmol) in CH₂Cl₂ (15 mL) was stirred in the dark for 1 hour. After filtration through diatomaceous earth and *in vacuo* concentration to 2 mL, addition of hexane (10 mL) caused the precipitation of 1H(OTf) as a microcrystalline green solid, which was washed with hexane and dried under vacuum. Yield: 0.082g, 86%. Anal. Calcd. for C₂₃H₂₀F₃MoN₃O₆S: C, 44.60; H, 3.25; N, 6.78. Found: C, 44.82; H, 3.12; N, 6.80. IR (CH₂Cl₂)νCO (cm⁻¹): 1956 vs, 1864 s. ¹H RMN(CD₂Cl₂): 10.80 [s_{br}, 1H, O-H], 9.30 [s_{br}, 2H, H₆ py_{coord}], 8.91 [d (4.5), 1H, H₆ py_{unc}], 8.17 [s_{br}, 2H, H₃ and H₄ py_{unc}], 8.04 [m, 2H, H₃ py_{coord}], 7.90 [t (7.8), 2H, H₄ py_{coord}], 7.58 [m, 1H, H₅ py_{unc}], 7.51 [m, 2H, H₅ py_{coord}], 3.49 [s, 2H, H_{syn}], 1.60 [s, 2H, H_{anti}], 1.57 [s, 3H, CH₃ of methallyl]. ¹³C{¹H} NMR(CD₂Cl₂): 227.0 [s, CO], 157.2 [s, py], 154.1 [s, py], 148.0 [s, py], 140.7 [s, py], 138.8 [s, py], 125.0 [s, py], 125.0 [s, py], 124.7 [s, py], 124.1 [s, py], 120.0 [c (J(C,F)= 319.6), CF₃ of OTf], 85.5 [s, C-OH], 84.5 [s, C_c of methallyl], 57.2 [s, C_t of methallyl], 19.3 [s, CH₃ of methallyl].

[Mo(η³-methallyl)(CO)₂(OC(py)₃)] (1). K[N(SiMe₃)₂] (0.9 mL of 0.5M solution in toluene, 0.45 mmol) was slowly added to a solution of 1H(OTf) (0.260g, 0.45 mmol) in THF (10 mL) at -78 °C and the mixture was stirred for 15 min. After *in vacuo* evaporation to dryness, the orange residue was extracted with CH₂Cl₂, filtered through a silicagel packed column and evaporated to dryness under vacuum. By slow diffusion of hexane into a concentrated solution of **1** in THF at -20°C orange crystals of X-ray quality were obtained. Yield: 0.082g, 86%. Anal. Calcd. for C₂₂H₁₉MoN₃O₃·C₄H₈O: C, 57.68; H, 5.03; N, 7.76. Found: C, 57.44; H, 5.21; N, 8.06. IR (CH₂Cl₂)νCO (cm⁻¹): 1918 vs, 1820 s. ¹H RMN(CD₂Cl₂): 9.09 [s_{br}, 2H, H₆ py_{coord}], 8.82 [s_{br}, 1H, H₆ py_{unc}], 8.35 [s_{br}, 1H, H₃ py_{unc}], 8.15 [s, 2H, H₃ py_{coord}], 7.89 [m, 1H, H₄ py_{unc}], 7.65 [m, 2H, H₄ py_{coord}], 7.37 [m, 1H, H₅ py_{coord}], 7.22 [m, 2H, H₅ py_{coord}], 3.20 [s, 2H, H_{syn}], 1.42 [s, 3H, CH₃ of methallyl], 1.37 [s, 2H, H_{anti}]. ¹³C{¹H} NMR(CD₂Cl₂): 232.3 [s, CO], 166.1 [s, py], 162.6 [s, py], 152.5 [s, py], 147.1 [s, py], 138.5 [s, py], 137.1 [s, py], 124.1 [s, py], 122.4 [s, 2C, py], 121.9 [s, py], 88.3 [s, C-O], 82.6 [s, C_c of methallyl], 55.4 [s, C_t of methallyl], 19.4 [s, CH₃ of methallyl]. Compound **1** can be synthesised either from **1H** or **1H(OTf)**, however the purification is easier when we started from **1H(OTf)**, since the triflate subproducts are retained in the

silicagel column.

[Mo(η^3 -methallyl)(CO)₂(HOC(Ph)(py)₂)] [BAr'₄] (1'H). This compound was synthesized in a similar way than 1H, starting from [MoCl(η^3 -methallyl)(CO)₂(NCMe)₂] (0.100 g, 0.308 mmol), HOC(Ph)(py)₂ (0.081 g, 0.308 mmol) and NaBAr'₄ (0.273 g, 0.308 mmol) in CH₂Cl₂ (15 mL). By slow diffusion of hexane (20 mL) into a concentrated solution of 1'H in CH₂Cl₂ at -20 °C red crystals of good quality for the determination of the structure by X-ray analysis were obtained. Yield: 0.370g, 90%. Anal. Calcd. for C₅₅H₃₃BF₂₄MoN₂O₃: C, 49.57; H, 2.50; N, 2.10. Found: C, 49.75; H, 2.40; N, 2.25. IR (CH₂Cl₂)vCO (cm⁻¹): 1955 vs, 1869 s; (KBr) vCO (cm⁻¹): 1956 f, 1875 f. ¹H RMN(CD₂Cl₂): 9.34 [s_{br}, 2H, H₆ py], 7.94 [td (7.8, 1.5), 2H, py], 7.82 [s, 9H, H_o of BAr'₄ and C-OH], 7.68-7.63 [m, 11H, H_p of BAr'₄, Ph and py], 7.53 [m, 2H, py], 3.39 [s, 2H, H_{syn}], 1.93 [s, 2H, H_{anti}], 1.67 [s, 3H, CH₃ of methallyl]. ¹³C RMN CD₂Cl₂: 227.4 [s, CO], 161.7 [c (J(C,B)= 49.7), C_i of BAr'₄], 156.8 [s, py], 154.4 [s, Ph], 141.2 [s, py], 134.8 [s, C_o of BAr'₄], 132.5 [s, Ph], 131.7 [s, py], 129.9 [s, Ph], 129.5 [s, Ph], 128.7 [m, C_m of BAr'₄], 125.4 [s, py], 124.6 [s, py], 124.5 [c (J(C,F)= 272.3), CF₃ of BAr'₄], 117.5 [s, C_p of BAr'₄], 88.6 [s, C-OH], 85.9 [s, C_c of methallyl], 57.0 [s, C_t of methallyl], 19.5 [s, CH₃ of methallyl].

[Mo(η^3 -methallyl)(CO)₂(HOC(py)₃)] [BAr'₄]-THF (1H-THF). A solution of 1H (0.200g, 0.15 mmol) in 15 mL of CH₂Cl₂ was added THF (1 mL) and the orange solution was stirred for 15 min. *In vacuo* concentration to a volume of 5 mL, and slow diffusion of hexane (10 mL) at -20 °C afforded orange crystals, one of which was used for a X-ray analysis. Yield: 0.190g, 90%. Anal. Calcd. for C₅₈H₄₀BF₂₄MoN₃O₄: C, 49.56; H, 2.87; N, 2.99. Found: C, 49.43; H, 2.95; N, 3.12. IR (CH₂Cl₂)vCO (cm⁻¹): 1956 vs, 1869 s; (KBr) vCO (cm⁻¹): 1958 f, 1873 f. ¹H RMN (CD₂Cl₂): 11.31 [s_{br}, 1H, O-H], 9.44 [s, 2H, H₆ py_{coord}], 8.91 [s_{br}, 1H, H₆ py_{unc}], 8.20 [s_{br}, 1H, H₄ py_{unc}], 8.06 [t (7.8), 2H, H₄ py_{coord}], 8.00 [s, 8H_o of BAr'₄], 7.89 [t (7.6), 3H, H₃ py_{coord} and py_{unc}], 7.75 [s, 4H, H_p of BAr'₄], 7.57 [t (6.0), 1H, H₅ py_{unc}], 7.52 [t (6.0), 2H, H₅ py_{unc}], 3.50 [s, 2H, H_{syn}], 3.43 [s_{br}, 4H, THF], 1.78 [s, 2H, H_{anti}], 1.75 [s_{br}, 4H, THF], 1.67 [s, 3H, CH₃ of methallyl]. ¹³C{¹H} NMR(CD₂Cl₂): 227.6 [s, CO], 162.0 [c (J(C,B)= 49.8), C_i of BAr'₄], 156.7 [s, py], 154.1 [s, py], 154.0 [s, py], 148.6 [s, py], 141.0 [s, py], 138.6 [s, py], 134.9 [s, C_o of BAr'₄], 129.2 [m, C_m of BAr'₄], 125.4 [s, py], 125.3 [s, py], 124.8 [c (J(C,F)= 272.3), CF₃ of BAr'₄], 124.3 [s, py], 117.7 [s, C_p of BAr'₄], 85.7 [s, C-OH], 85.0 [s, C_c of methallyl], 68.0 [s, THF], 56.9 [s, C_t of methallyl], 25.1 [s, THF], 19.3 [s, CH₃ of methallyl].

[Mo(η^3 -methallyl)(CO)₂(HOC(py)₃)] [BAr'₄]-DMPU (1H-DMPU). It was synthesized in a similar way than 1H-THF, from 1H (0.250 g, 0.18 mmol) and DMPU (25 μ L, 0.20 mmol) in CH₂Cl₂ (15 mL). After 1 hour stirring, the solvent was removed under vacuum and the orange solid was washed with hexane (3 x 5 mL). Orange crystals of quality for the structure

determination by x-ray analysis were obtained by slow diffusion at -20 °C of hexane (20 mL) into a concentrated solution of **1H**-DMPU in CH₂Cl₂. Yield: 0.260g, 85%. Anal. Calcd. for C₆₀H₄₄BF₂₄MoN₅O₄·2CH₂Cl₂: C, 47.71; H, 3.10; N, 4.49. Found: C, 47.49; H, 2.85; N, 4.90. IR (CH₂Cl₂)vCO (cm⁻¹): 1952 vs, 1864 s, 1558 m_{DMPU}; (KBr) vCO (cm⁻¹): 1954 f, 1873 f; vCO (cm⁻¹)_{DMPU} 1559 m. ¹H NMR(CD₂Cl₂): 9.30 [s, 2H, H₆ py_{coord}], 8.87 [s br, 1H, H₆ py_{unc}], 8.11 [s br, 2H, H₄ py_{coord}], 8.02 [m, 1H, H₄ py_{unc}], 7.88 [m, 2H, H₃ py_{coord}], 7.84 [m, 1H, H₃ py_{unc}], 7.75 [s, 8H_o of BAR'₄], 7.54 [m, 7H, H_p of BAR'₄, H₅ py_{coord} and py_{unc}], 3.36 [s, 2H, H_{syn}], 3.12 [t(5.9), 4H, DMPU], 2.48 [s, 6H, DMPU], 1.85 [m, 2H DMPU], 1.63 [s, 2H, H_{anti}], 1.58 [s, 3H, CH₃ of methallyl]. ¹³C{¹H} NMR(CD₂Cl₂): 230.1 [s, CO], 164.5 [c (J(C,B)= 49.8), C_i of BAR'₄], 160.3 [s, py], 159.2 [s, CO DMPU], 157.6 [s, py], 156.2 [s, py], 150.9 [s, py], 143.1 [s, py], 140.3 [s, py], 137.2 [s, C_o of BAR'₄], 131.3 [m, C_m of BAR'₄], 127.9 [s, py], 127.2 [s, py], 127.0 [s, py], 126.9 [c (J(C,F)= 272.3), CF₃ of BAR'₄], 126.8 [s, py], 119.9 [s, C_p of BAR'₄], 87.6 [s, C-OH], 87.3 [s, C_c of methallyl], 59.2 [s, C_t of methallyl], 49.8, 37.6, 23.4 [s, DMPU], 21.6 [s, CH₃ of methallyl].

[Mo(η³-methallyl)(CO)₂(HOC(py)₃)](BAR'₄)·py (1H-py). Compound **1H-py** was prepared as describe above for **1H**-THF, starting from **1H** (0.100 g, 0.075 mmol) and py (6 μL, 0.075 mmol). Orange crystals of **1H-py** were obtained by slow diffusion of hexane into a concentrated CH₂Cl₂ solution at -20 °C. Yield: 0.086 g, 82%. Anal. Calcd. for C₅₉H₃₇BF₂₄MoN₄O₃: C, 50.16; H, 2.64; N, 3.97. Found: C, 50.28; H, 2.45; N, 3.75. IR (CH₂Cl₂)vCO (cm⁻¹): 1945 vs, 1856 s; (KBr) vCO (cm⁻¹): 1945 f, 1859 f. ¹H RMN(CD₂Cl₂): 12.90 [s_{br}, 1H, O-H], 9.28 [s, 2H, H₆ py_{coord}], 8.67 [d (4.2), 1H, H₆ py_{unc}], 8.03 [m, 2H, py], 7.87 [m, 7H, py], 7.76 [s, 8H_o of BAR'₄], 7.59 [s, 4H, H_p of BAR'₄], 7.48 [m, 5H, py], 3.25 [s, 2H, H_{syn}], 1.65 [s, 3H, CH₃ of methallyl], 1.57 [s, 2H, H_{anti}], ¹³C{¹H} NMR(CD₂Cl₂): 228.5 [s, CO], 162.1 [c (J(C,B)= 49.8), C_i of BAR'₄], 159.7 [s, py], 156.7 [s, py], 153.6 [s, py], 148.6 [s, py], 143.6 [s, py], 141.9 [s, py], 140.5 [s, py], 138.2 [s, py], 134.8 [s, C_o of BAR'₄], 129.4 [m, C_m of BAR'₄], 126.2 [s, py], 125.6 [c (J(C,F)= 272.3), CF₃ of BAR'₄], 124.6 [s, py], 124.3 [s, py], 121.2 [s, py], 117.4 [s, C_p of BAR'₄], 86.4 [s, C-OH], 84.7 [s, C_c of methallyl], 56.4 [s, C_t of methallyl], 19.6 [s, CH₃ of methallyl].

[Mo(η³-methallyl)(CO)₂(HOC(py)₃)](BAR'₄)·TEA (1H-TEA). It was synthesized in a similar way than **1H**-THF, starting from **1H** (0.150 g, 0.112 mmol) and TEA (16 μL, 0.112 mmol). By slow diffusion on hexane into a concentrated solution of in CH₂Cl₂ orange crystals were obtained for an X-ray analysis. Yield: 0.126 g, 78%. Anal. Calcd. for C₆₀H₄₇BF₂₄MoN₄O₃: C, 50.23; H, 3.30; N, 3.90. Found: C, 50.36; H, 2.95; N, 3.80. IR (CH₂Cl₂)vCO (cm⁻¹): 1930 vs, 1837 s; (KBr) vCO (cm⁻¹): 1933 f, 1844 f. ¹H RMN (CD₂Cl₂): 9.90 [s_{br}, 1H, O-H], 9.23 [s, 2H, H₆ py_{coord}], 8.76 [s, 1H, H₆ py_{unc}], 7.91 [t (7.8), 1H, H₄ py_{unc}], 7.82 [s, 8H_o of BAR'₄], 7.76 [d (6.9), 2H, H₄ py_{unc}], 7.62 [s, 7H, H_p of BAR'₄, H₃ py_{coord} and py_{unc}], 7.47 [t (6.5), 2H, H₅ py_{coord}],

7.33 [t(6.3), 2H, H_5 py_{coord}], 3.48 [s, 2H, H_{syn}], 2.67 [m, 6H, CH_2 of TEA], 1.66 [s, 3H, CH_3 of methallyl], 1.54 [s, 2H, H_{anti}], 1.01 [t(7.2), 9H, CH_3 of TEA]. $^{13}C\{^1H\}$ NMR(CD₂Cl₂): 230.5 [s, CO], 161.8 [c (J(C,B)= 49.8), C_i of BAr'₄], 152.6 [s, py], 149.9 [s, py], 148.6 [s, py], 147.8 [s, py], 139.4 [s, py], 139.2 [s, py], 134.9 [s, C_o of BAr'₄], 129.0 [m, C_m of BAr'₄], 126.0 [s, py], 124.6 [c (J(C,F)= 272.3), CF_3 of BAr'₄], 124.5 [s, py], 123.8 [s, py], 122.2 [s, py], 117.5 [s, C_p of BAr'₄], 89.4 [s, C-OH], 84.0 [s, C_c of methallyl], 56.0 [s, C_t of methallyl], 45.2 [s, CH_2 of TEA], 19.7 [s, CH_3 of methallyl], 7.9 [s, CH_3 of TEA].

[Mo(η^3 -methallyl)(CO)₂(HOC(py)₃)]BAr'₄·DBU (1H-DBU). DBU (23 μ L, 0.17 mmol) was added to a solution of **1H** (0.200 g, 0.15 mmol) in CH₂Cl₂ (15 ml) causing orange solution darkness. After stirring for 30 min., the solution was *in vacuo* dried. The residue was washed with hexane (3 x 10 mL), solved in diethylether (10 mL), layered with hexane (25 mL) and placed at -20 °C, affording deep orange crystals, one of which was used for an X-ray analysis. Yield: 0.190 g, 85 %. Anal. Calcd. for C₆₃H₄₈BF₂₄MoN₅O₃: C, 50.83; H, 3.25; N, 4.71. Found: C, 50.59; H, 2.90; N, 4.95. IR (CH₂Cl₂) ν CO (cm⁻¹): 1927 vs, 1932 s; (KBr) ν CO (cm⁻¹): 1929 f, 1843 f. 1H RMN CD₂Cl₂: 11.54 [s, 1H, OH], 9.12 [s br, 2H, H_6 py_{coord}], 8.75 [s, 1H, H_6 py_{unc}], 7.84 [s, 18H of BAr'₄, H_4 and H_3 of py], 7.33 [m, 3H, H_5 py_{coord} and py_{unc}], 3.35-1.31 [23H, DBU and methallyl]. $^{13}C\{^1H\}$ NMR(CD₂Cl₂): 231.7 [s, CO], 165.4 [s, py], 162.0 [s, py], 161.7 [c (J(C,B)= 49.8), C_i of BAr'₄], 152.5 [s, py], 147.5 [s, py], 138.7 [s, py], 137.1 [s, 2C py], 134.8 [s, C_o of BAr'₄], 128.9 [m, C_m of BAr'₄], 124.6 [c (J(C,F)= 272.3), CF_3 of BAr'₄], 124.1 [s, py], 122.7 [s, 2C py], 117.5 [s, C_p of BAr'₄], 88.9 [s, C-OH], 82.7 [s, C_c of methallyl], 55.4 [s, C_t of methallyl], 54.3, 48.4, 37.5, 32.2, 28.7, 26.4, 23.8, 19.5 [s, DBU], 19.3 [s, CH_3 of methallyl].

Crystal Structure Determination. General Description: Diffraction data for **1H**, **1H-THF**, **1H-DMPU** and **1H-DBU** were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo-K α radiation. A semi-empirical absorption correction was performed with

SORTAV.⁵ Diffraction data for **1**, **1'H**, **1H-py** and **1H-TEA** were collected on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED (Oxford Diffraction Ltd., 2006).⁶ Structures were solved by Patterson interpretation using the program DIRDIF.⁷ Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.⁸ X-H hydrogen atom positions (X = O, N) were located in the corresponding Fourier difference maps and were refined riding on their

parent atoms with $-1.2 U_{eq}$ thermal parameters and restricted X–H bond distances. All the other hydrogen atoms were set in calculated positions and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.⁹ The WINGX program system¹⁰ was used throughout the structure determinations. In some of the structures fluorine atoms are affected by some degree of disorder, and therefore, their U_{eq} are abnormally high. This is a very common feature of the trifluoromethyl groups of the BAr'_4 anion.

CCDC deposition numbers: 786107 (**1H**), 786108 (**1**), 786109 (**1H-THF**), 786110 (**1H-DBU**), 786111 (**1H-DMPU**), 786112 (**1H-py**), 786113 (**1H-TEA**) and 786114 (**1'H**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 2S: Thermal ellipsoid (30%) plot of the cation in **1H-DMPU**.

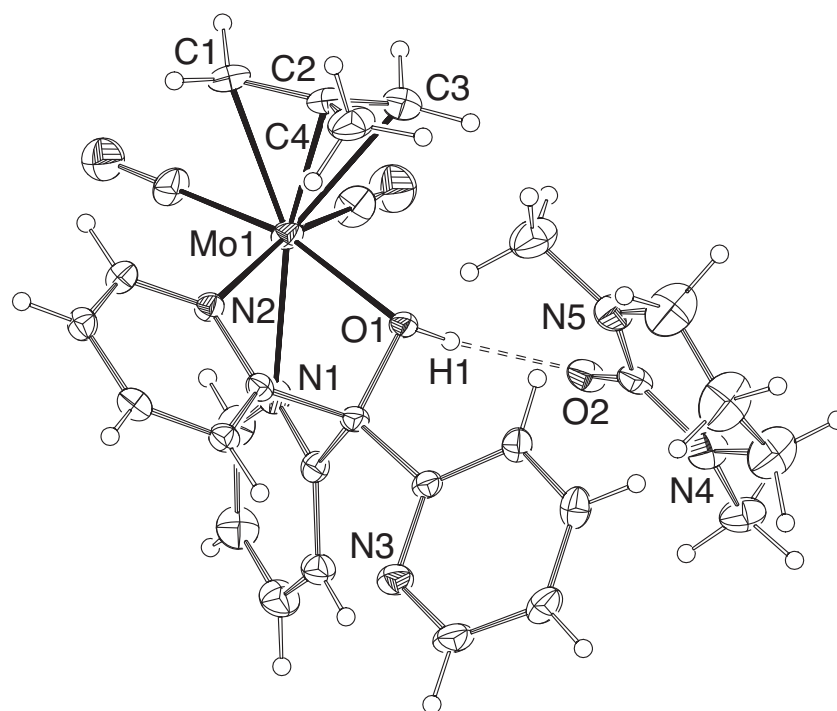


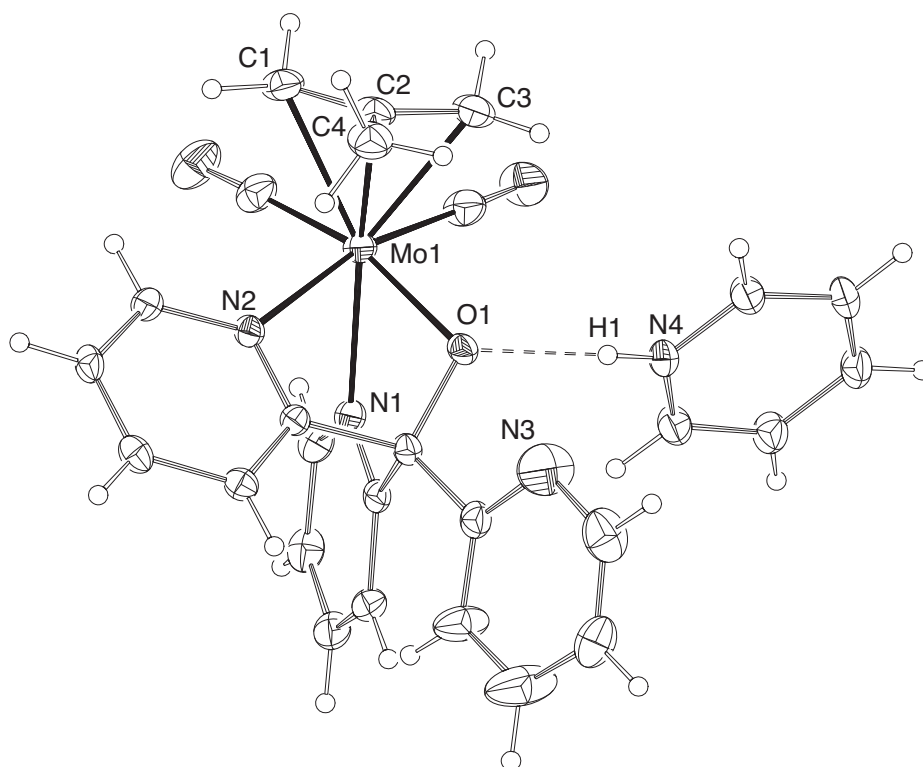
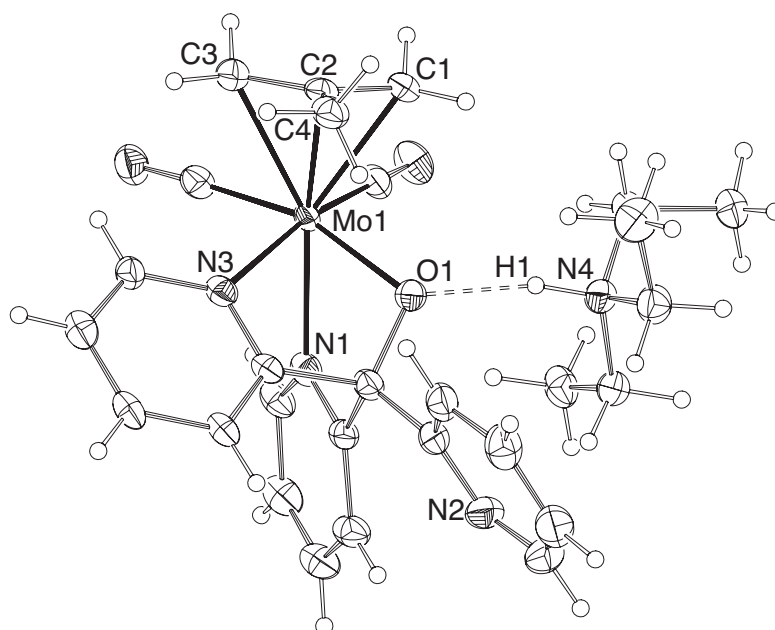
Figure 3S: Thermal ellipsoid (30%) plot of the cation in **1H-py**.**Figure 4S:** Thermal ellipsoid (30%) plot of the cation in **1H-TEA**.

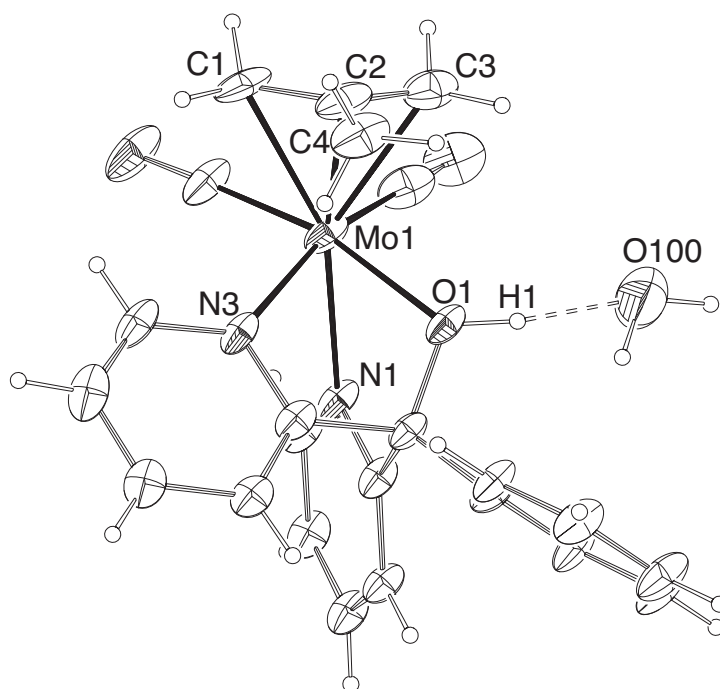
Figure 5S: Thermal ellipsoid (30%) plot of the cation in **1'H**.

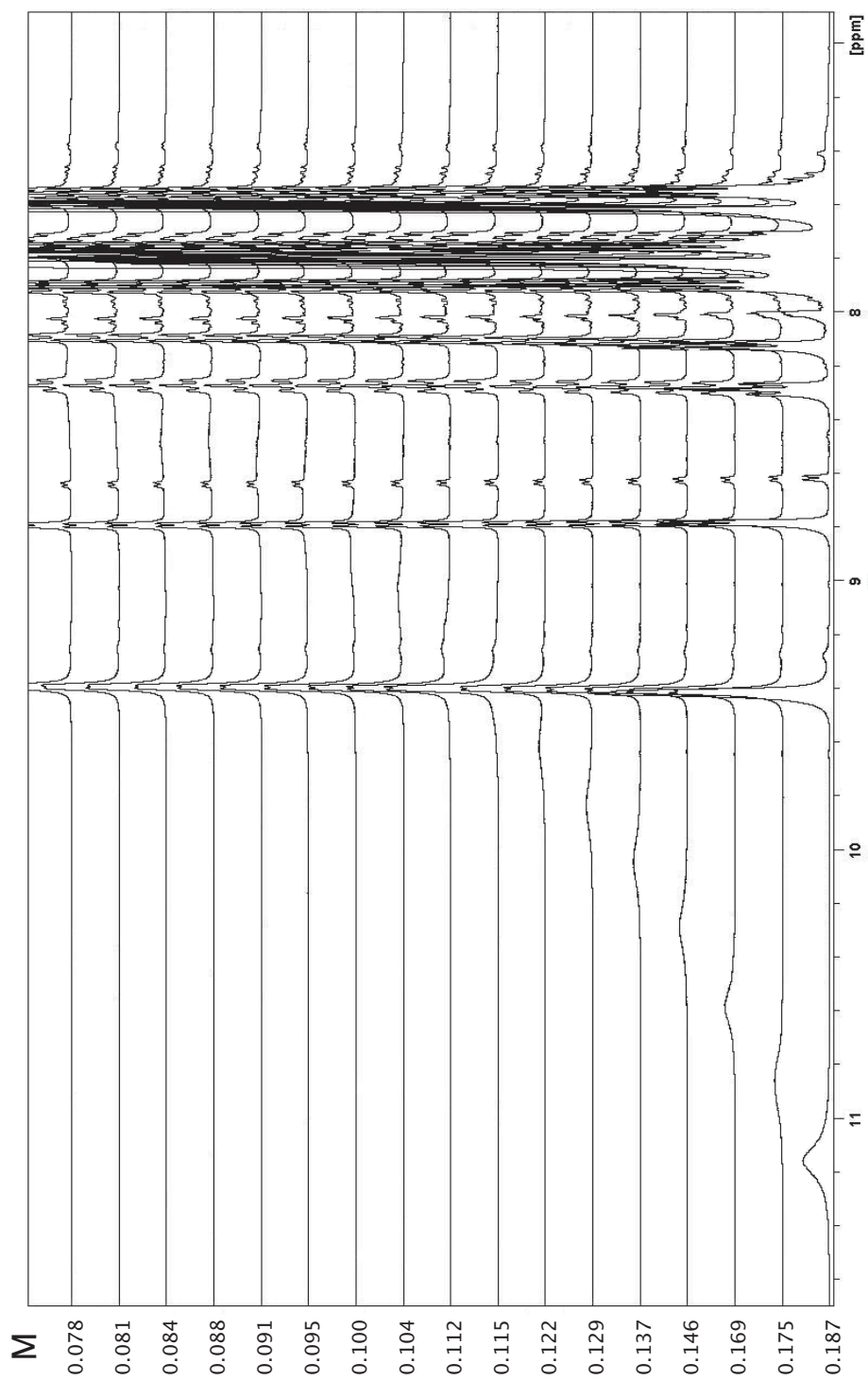
Figure 6S: ^1H NMR (CD_2Cl_2) of 1H at different concentrations.

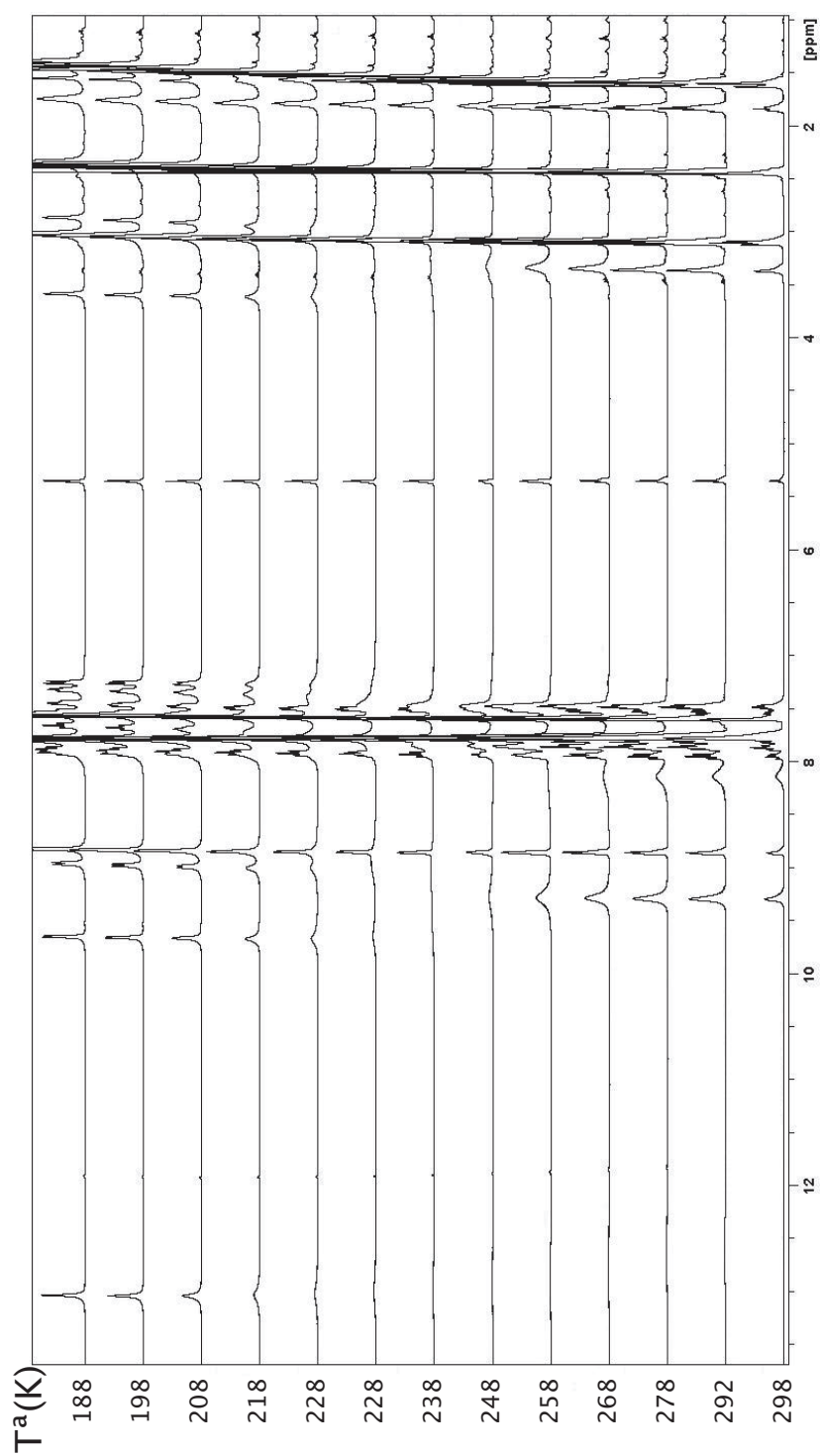
Figure 7S: VT ^1H NMR (CD_2Cl_2) of 1H-DMPU.

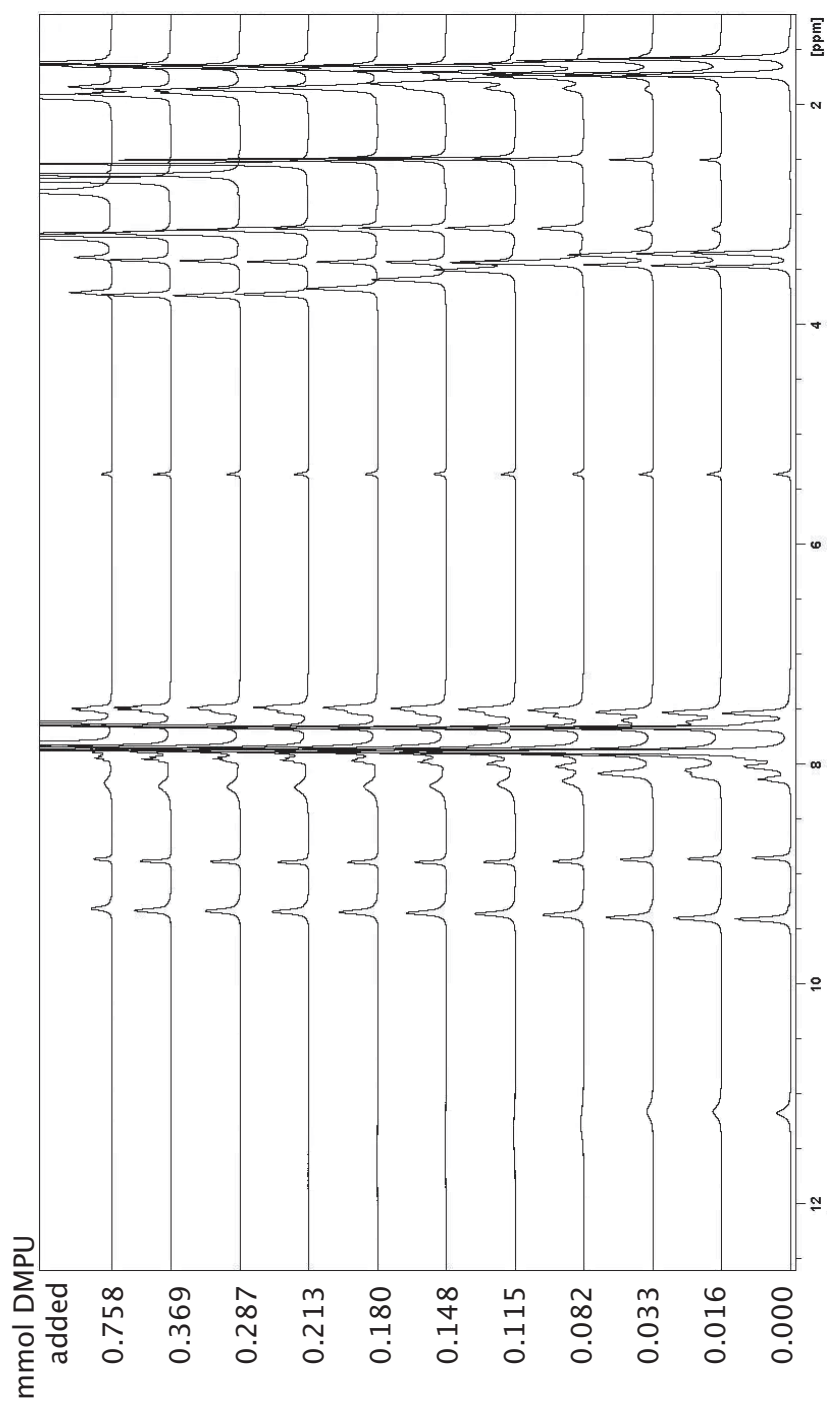
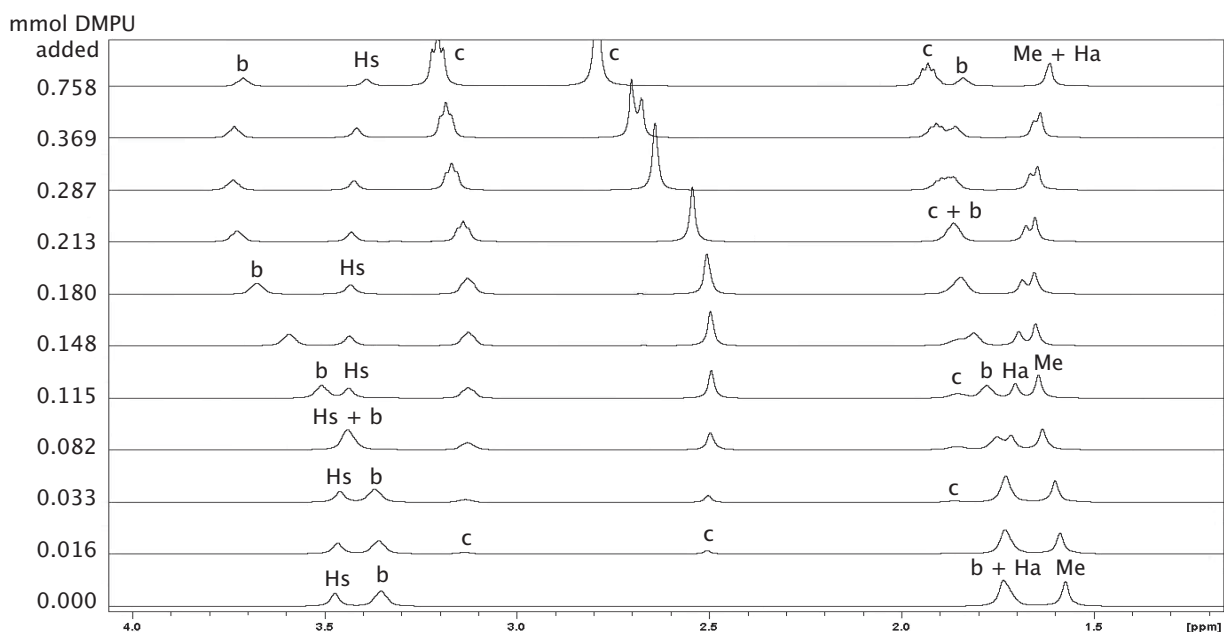
Figure 8S: ^1H NMR in CD_2Cl_2 of the displacement of THF in **1H**-THF after DMPU addition.

Figure 9S: Amplified section (4-1.2 ppm) of the spectra showed above.

b= THF; c= DMPU; Hs, Ha and Me are methallyl signals

References

- ¹ H. Tom Dieck, H. Friedel, *J. Organomet. Chem.*, **1968**, *14*, 375-385.
- ² M. Brookhart, B. Grant, A. F. Jr. Volpe, *Organometallics*, **1992**, *11*, 3920-3922.
- ³ R. T. Jonas, T. D. P. Stack, *Inorg. Chem.*, **1998**, *37*, 6615-6629.
- ⁴ R. K. Boggess, C. E. Heltzell, *Inorg. Chem.*, **1985**, *24*, 2947-2950.
- ⁵ R. H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-38.
- ⁶ *CrysAlisPro RED*, version 1.171.31.7; Oxford Diffraction Ltd.: Oxford, UK, 2009.
- ⁷ P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. García-Granda, R. O. Gould, *The DIRDIF Program System*, version 2008.3; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 2008.
- ⁸ G. M. Sheldrick, *SHELXL*, version 2008. *Acta Cryst.* **2008**, *A64*, 112.
- ⁹ A. L. Spek, *PLATON version 1.15: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2008.
- ¹⁰ L. J. Farrugia, *J. Appl. Crystallogr.*, **1999**, *32*, 837.