Unexpected Chemoselectivity in the Schiff Condensation of Amines with $\eta^2(C,O)$-$\eta^1(O)$-Coordinated Aldehyde

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Supporting Information

Table of contents

Experimental Section S1
Materials and general methods S1
Synthesis of $[\text{Cr}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2a) S2
Synthesis of $[\text{Mo}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2b) S2
Synthesis of $[\text{W}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2c) S2
Reaction of compound $[\text{Mo}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2b) with $\text{H}_2\text{N}^{\text{n}}\text{Bu}$. S2
Reaction of compound $[\text{Mo}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2b) with $\text{H}_2\text{NCH}_2\text{Ph}$. S2
Reaction of compound $[\text{Mo}_2(\text{CO})_6(\text{pyC}(\text{H})=\text{O})_2]$ (2b) with $\text{H}_2\text{N}^{\text{t}}\text{Bu}$. S3
Synthesis of $[\text{Mo}(\text{CO})_4(\text{pyC}(\text{H})=\text{O})]$ (3) S3
Reaction of compound $[\text{Mo}(\text{CO})_4(\text{pyC}(\text{H})=\text{O})]$ (3) with $\text{H}_2\text{N}^{\text{n}}\text{Bu}$. S3
Reaction of compound $[\text{Mo}(\text{CO})_4(\text{pyC}(\text{H})=\text{O})]$ (3) with $\text{H}_2\text{NCH}_2\text{Ph}$. S3
Reaction of compound $[\text{Mo}(\text{CO})_4(\text{pyC}(\text{H})=\text{O})]$ (3) with $\text{H}_2\text{N}^{\text{t}}\text{Bu}$. S3
Reaction of compound $[\text{Mo}(\text{CO})_4(\text{pyC}(\text{H})=\text{O})]$ (3) with $\text{H}_2\text{NPh}$. S3
Figure S1: $^1\text{H}$ NMR (300.13 MHz, THF-$d_8$) spectrum of compound 2b S4
Figure S2: $^1\text{H}$ NMR (300.13 MHz, THF-$d_8$) spectrum of compound 4a S4
Figure S3: $^1\text{H}$ NMR (400.13 MHz, acetone-$d_6$) spectrum of compound 4b S5
Figure S4: $^1\text{H}$ NMR (400.13 MHz, acetone-$d_6$) spectrum of compound 4d S5
Figure S5: IR spectrum in THF of compound 2a S6
Figure S6: IR spectrum in THF of compound 2b S6
Figure S7: IR spectrum in THF of compound 2c S7
Figure S8: Thermal ellipsoid plots (30 %) of the structure of complex 2a. S7
Figure S9: Thermal ellipsoid plots (30 %) of the structure of complex 2c. S8

Experimental Section

Materials and general methods

All operations were performed under an atmosphere of dry nitrogen using Schlenk and vacuum techniques. Dichloromethane and acetonitrile were distilled from CaH$_2$. THF and diethylether were distilled from Na/benzophenone. Hexane was distilled from Na. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated. IR spectra in solution were recorded with a Perkin Elmer Spectrum RX I FT-IR instrument,
using cells with CaF$_2$ windows. All NMR solvents were stored over molecular sieves and degassed prior to use. $^1$H NMR experiments were measured on a Bruker AV400 and ARX300 spectrometers. Chemical shift values are given in ppm. $^1$H NMR chemical shifts are referenced to TMS, using solvents as an internal reference.

**Synthesis of [Cr$_6$(CO)$_6$] (py(H)=O)$_2$ (2a)**

To a solution of pyridine-2-carbaldehyde (0.071 g, 0.66 mmol) in THF (40 mL) was added [Cr(C$_2$H$_4$)$_2$(CO)$_2$] (1a) (0.171 g, 0.66 mmol). The mixture was stirred for 20 min. After that, the green solution was concentrated in vacuo, layered with hexane (20 mL) and stored at -20 °C to afford black crystals of 2a, one of which was used for X-ray analysis. Yield 0.130 g, 81%. Anal. Calcd. for C$_{6}$H$_{6}$Cr$_{3}$N$_{3}$O$_{6}$: C 37.51, H 1.64, N 4.79%. IR (THF), ν(CO): 1984 vs, 1928 vs, 1904 s, 1963 vs, 1844 vs cm$^{-1}$. IR (KBr), ν(CO): 1973 vs, 1923 vs, 1899 vs, 1867 vs 1849 vs cm$^{-1}$.

**Synthesis of [Mo$_2$(CO)$_6$](py(H)=O)$_2$ (2b)**

A solution of [Mo(CO)$_6$] (0.200 g, 0.76 mmol) in acetonitrile (20 mL) was refluxed for 3 h to form [Mo(C$_2$H$_4$CN)$_4$(CO)$_3$] (1b). Following the removal of solvent, a solution of pyridine-2-carbaldehyde (0.081 g, 0.76 mmol) in THF (30 mL) was added to the crude pale yellow solid. The mixture immediately turned deep green and it was stirred for 5 min. Addition of hexane and slow solvents evaporation at reduced pressure gave compound 2b as dark green microcrystals. Yield 0.203 g, 93%. Anal. Calcd. for C$_{3}$H$_{15}$Mo$_3$O$_{12}$: C 37.65, H 1.76, N 4.88. Found: C 37.51, H 1.64, N 4.79%. IR (THF), ν(CO): 1987 vs, 1925 s cm$^{-1}$. IR (Nujol), ν(CO): 1984 vs, 1928 vs, 1904 s, 1899 vs, 1867 vs cm$^{-1}$. IR (KBr), ν(CO): 1977 vs, 1926 vs, 1890 s cm$^{-1}$.

**Synthesis of [W$_2$(CO)$_6$](py(H)=O)$_2$ (2c)**

To a solution of pyridine-2-carbaldehyde (0.041 g, 0.38 mmol) in THF (30 mL) was added [Cr(C$_2$H$_4$)$_2$(CO)$_2$] (2a) and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound 2c as brown microcrystals. Yield 0.240 g, 85%. Anal. Calcd. for C$_{3}$H$_{15}$Mo$_3$O$_{12}$: C 37.65, H 1.64, N 4.79%. IR (Nujol), ν(CO): 1980 vs, 1921 vs, 1894 vs cm$^{-1}$. 1H NMR (300.13 MHz, THF-d$_8$) δ = 8.71 [d (5), 1H, pyH$_3$]. 8.06 [td (8, 2), 1H, pyH$_3$], 7.84 [d (8), 1H, pyH$_3$]. 7.46 [m, 1H, pyH$_3$]. 6.62 [s, 1H, pyH=O].

**Reaction of compound [Mo$_2$(CO)$_6$](py(H)=O)$_2$ (2b) with H$_2$N$^+$Bu.**

To a freshly prepared solution of [Mo$_2$(CO)$_6$](py(H)=O)$_2$ (2b) (0.218 g, 0.38 mmol), H$_2$N$^+$Bu (0.056 g, 0.76 mmol) was added and stirred at room temperature under CO atmosphere during 15 min. The solvents were evaporated in vacuo, and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH$_2$Cl$_2$ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)$_6$](py(CH)=N$^+$Bu)$_2$ (4a) as brown microcrystals. Yield 0.240 g, 85%. Anal. Calcd. for C$_{3}$H$_{15}$Mo$_3$O$_{12}$: C 42.83, H 3.81, N 7.57. Found: C 42.81, H 3.70, N 7.33%. IR (THF), ν(CO): 1979 vs, 1923 vs, 1895 vs cm$^{-1}$. IR (KBr), ν(CO): 1975 vs, 1923 vs, 1894 vs cm$^{-1}$. 1H NMR (300.13 MHz, THF-d$_8$) δ = 8.83 [d (5), 1H, pyH$_3$]. 8.19 [d (8, 2), 1H, pyH$_3$]. 7.76 [m, 1H, pyH$_3$]. 6.77 [m, 1H, pyH$_3$]. 4.07 [q (7), 2H, NCH$_2$CH$_2$CH$_2$], 2.05 [q (7), 2H, NCH$_2$CH$_2$CH$_2$], 1.39 [m, 2H, NCH$_2$CH$_2$CH$_2$], 0.99 [s, (7), 3H, CH$_3$]. 1H NMR (300.13 MHz, THF-d$_8$) δ = 9.08 [d (5), 1H, pyH$_3$], 8.63 [s, 1H, pyH=O], 8.01 [td (2, 1H, pyH$_3$)], 7.91 [d (8), 1H, pyH$_3$], 7.52 [m, 1H, pyH$_3$], 4.02 [q (7), 2H, NCH$_2$CH$_2$CH$_2$], 2.02 [m, 2H, NCH$_2$CH$_2$CH$_2$], 1.38 [m, 2H, NCH$_2$CH$_2$CH$_2$], 1.00 [t (7), 3H, CH$_3$].

**Reaction of compound [Mo$_2$(CO)$_6$](py(H)=O)$_2$ (2b) with H$_2$NCH$_2$Ph.**

To a freshly prepared solution of [Mo$_2$(CO)$_6$](py(H)=O)$_2$ (2b) (0.218 g, 0.38 mmol), H$_2$NCH$_2$Ph (0.083 g, 0.76 mmol) was added and stirred at room temperature under CO atmosphere during 15 min. The solvents were evaporated in vacuo, and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH$_2$Cl$_2$ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)$_6$](py(CH)=NCH$_2$Ph) (4b) as red dark microcrystals. Yield 0.267 g, 87%. Anal. Calcd. for C$_{3}$H$_{15}$Mo$_3$O$_{12}$: C 44.65, H 2.07, N 5.74. Found: C 44.65, H 1.98, N 5.51%. IR (THF), ν(CO): 1979 vs, 1923 vs, 1894 vs, 1867 vs, 1849 vs cm$^{-1}$. 1H NMR (400.13 MHz, Acetone-d$_6$) δ = 9.01 [s, (5), 1H, pyH$_3$], 8.34 [d, 1H, pyH$_3$], 7.66 [m, 1H, pyH$_3$], 7.49 [m, 2H, Ph], 7.42-7.32 [m, 3H, Ph], 5.26 [s, 2H, NCH$_2$].
Synthesis of [Mo(CO)₄(pyC(H)=O)] (3)

Pyridine-2-carbaldehyde (0.064 g, 0.60 mmol) was added to a solution of [Mo(CO)₄(NBD)]²⁻ (NBD = norbornadiene) (0.180 g, 0.60 mmol) in THF (20 mL). The color of the solution changed immediately from yellow to deep blue. The solution was stirred for 30 min. Addition of hexane and slow evaporation at reduced pressure gave compound 3 as black solid which was washed with hexane (2 x 15 mL). Yield 0.111 g, 59%. Anal. Calcd. for C₃₀H₂₄MoNO₄: C 57.10, H 2.94, N 7.36 %. Found: C 57.43, H 2.83, N 7.41 %. IR (THF), ν(CO): 2022 s, 1918 vs, 1893 sh, 1843 s cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 10.26 [s, 1H, pyC(H)=O], 9.22 [d(5), 1H, pyH'], 8.65 [d(8), 1H, pyH'], 7.97 [m, 1H, pyH'], 7.80 [m, 1H, pyH'], 7.78 [m, 1H, pyH'].

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NBu.

To a solution of H₂NBu (0.017 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NBU)] (4a) as brown microcrystals. Yield 0.055 g, 65%.

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NCH₂Ph.

To a solution of H₂NCH₂Ph (0.025 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NCH₂Ph)] (4b) as red microcrystals. Yield 0.060 g, 64%.

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NPh.

To a solution of H₂NPh (0.021 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compounds [Mo(CO)₄(pyC(H)=NPh)] (4d) as dark purple microcrystals. Yield 0.057 g, 64%. Anal. Calcd. for C₃₄H₁₈MoNO₄: C 72.35, H 2.97, N 7.22 %. Found: C 72.47, H 2.88, N 7.28 %. IR (THF), ν(CO): 2013 s, 1907 vs, 1894 sh, 1845 s cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 9.99 [s, 1H, pyC(H)=O], 9.19 [d(5), 1H, pyH'], 8.40 [dd(8, 2), 1H, pyH'], 5.80 [m, 1H, pyH'], 7.76 [m, 1H, pyH'].

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NPh.

To a solution of H₂NPh (0.021 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compounds [Mo(CO)₄(pyC(H)=NPh)] (4d) as dark red microcrystals. Yield 0.047 g, 55%.
Figure S1: $^1$H NMR (300.13 MHz, THF-d$_8$) spectrum of compound 2b.

Figure S2: $^1$H NMR (300.13 MHz, THF-d$_8$) spectrum of compound 4a.
Figure S3: $^1$H NMR (400.13 MHz, acetone-$d_6$) spectrum of compound 4b.

Figure S4: $^1$H NMR (400.13 MHz, acetone-$d_6$) spectrum of compound 4d.
Figure S5: IR spectrum in THF of compound 2a.

Figure S6: IR spectrum in THF of compound 2b.
Figure S7: IR spectrum in THF of compound 2c.

Figure S8: Thermal ellipsoid plots (30 % probability) of the structure of complex 2a.
Figure S9: Thermal ellipsoid plots (30 % probability) of the structure of complex 2c.