TGA of \(2a\)

\[
\begin{align*}
M_{2a} &= 585 \text{ g mol}^{-1} \\
M_{\text{CO}} &= 28 \text{ g mol}^{-1} \\
n_{\text{CO}} &= 3 \\
\text{expected for 3 CO: } \Delta m/m &= 100(n_{\text{CO}}M_{\text{CO}})/M = 14.4%.
\end{align*}
\]
TGA of 2b, 3b, 4b and 5b

Theoretical $\Delta m/m$ for 2b, 3b, 4b, 5b

$\Delta m/m = 100 \times \frac{n_{CO} \times M_{CO}}{M_{resin} + M_{complex \ fragment}}$

$M_{resin} \approx 1500 \text{ g mol}^{-1}$ for resin loading of 0.5 mmol ligand g$^{-1}$

$M_{CO} = 28 \text{ g mol}^{-1}$

2b: $n_{CO} = 3$; $M_{complex \ fragment} = 387 \text{ g mol}^{-1}$ $\Rightarrow \Delta m/m = 4.45\%$ (found 4.4%)

3b: $n_{CO} = 6$; $M_{complex \ fragment} = 774 \text{ g mol}^{-1}$ $\Rightarrow \Delta m/m = 7.39\%$ (found 7.7%)

4b: $n_{CO} = 7$; $M_{complex \ fragment} = 595 \text{ g mol}^{-1}$ $\Rightarrow \Delta m/m = 9.36\%$ (found 8.7%)

5b: $n_{CO} = 10$; $M_{complex \ fragment} = 982 \text{ g mol}^{-1}$ $\Rightarrow \Delta m/m = 11.28\%$ (found 11.2%)

$y = 0.9827x$

$R^2 = 0.9939$
UV/Vis spectra of 2b, 3b, 4b, 5b and PS-O-(N∩N’)Mo(CO)₄
(diffuse reflectance in polytetrafluoroethylene)

Solution phase Synthesis of 2a, 3a, 4a and 5a

2a: 1a (198 mg, 1 mmol) was treated with (CH₃CN)₃Mo(CO)₃ (303 mg, 1 mmol) in CH₃CN (100 mL) to give a deep blue solution. After stirring for 30 min (IR control) CN-(N∩N’) (207 mg, 1 mmol) dissolved in THF (40 mL) was added. The solution turned green immediately and was stirred until IR spectroscopy indicated complete transformation. The volume of the solution was reduced to ca. 10 ml and diethyl ether/hexanes were added. The green residue was dissolved in THF and again precipitated by adding diethyl ether/hexanes. The precipitate was washed with diethyl ether/hexanes and dried in vacuo giving a green powder (468 mg, 80%).

Calcd for C₂₈H₁₉N₅O₄Mo (585.4) C: 57.45, H: 3.27, N:11.96; found C: 56.62, H: 4.10, N:10.50.

Osmometry (THF): M = 616 g mol⁻¹.

MS (FAB): m/z = 587 (31, M⁺), 559 (100, M⁺-CO), 380 (95, M⁺-CN-(N∩N’)).

UV/Vis (THF): λ max (ε) = 613 (3475).

IR (THF): 2076 (m, CN), 1918 (vs, CO), 1855 (s, CO), 1824 (s, CO).

IR (CsI): 3388 (br, OH), 2089 (m, CN), 1911 (vs, CO), 1833 (s, CO), 1808 (s, CO).
$^1$H NMR (CD$_2$Cl$_2$): 6.97 (d, 2H, H$^3$, $^3$J$_{HH}$ = 8.8Hz), 7.3-7.7 (m, 8H, H$^2,6$, H$^{2',6'}$, H$^{3',5'}$, H$^{11}$, H$^{11'}$), 
7.8-8.0 (m, 3H, H$^7$, H$^{10}$, H$^{11}$), 8.2-8.3 (m, 1H, H$^9$), 8.59 (d, 1H, H$^{12'}$, $^3$J$_{HH}$ = 5.4Hz), 8.66 (s, 1H, H$^7$), 8.73 (bs, 1H, H$^7'$), 9.30 (d, 1H, H$^{12}$, $^3$J$_{HH}$ = 5.2Hz).

TG: $\Delta$m/m = 14.8% at 200°C; calcd for 3 CO: 14.4%.

3a: 2a (293 mg, 0.5 mmol) was treated with (CH$_3$CN)$_3$Mo(CO)$_3$ (152 mg, 0.5 mmol) in CH$_3$CN (50 mL) to give a dark solution. After stirring for 45 min (IR control) CN-(N∩N') (104 mg, 0.5 mmol) dissolved in THF (20 mL) was added giving a green solution. After stirring for 60 min (IR control) the volume of the solution was reduced to ca. 10 ml and diethyl ether was added giving a green precipitate and a slightly green solution containing mononuclear (ether soluble) complexes. The residue was repeatedly washed with diethyl ether until the ether remained colourless and dried in vacuo giving a green powder (394 mg, 81%).

Calcd for C$_{44}$H$_{28}$N$_8$O$_7$Mo$_2$ (972.6) C: 54.34, H: 2.90, N: 11.52; found C: 54.23, H: 3.95, N:10.40.

Osmometry (THF): M = 1015 g mol$^{-1}$.

UV/Vis (THF): $\lambda_{max}$ ($\varepsilon$) = 612 (10710).

IR (THF): 2077 (m, CN), 1917 (vs, CO), 1853 (s, CO), 1822 (s, CO).

IR (CsI): 3396 (br, OH), 2095 (m, CN), 1911 (vs, CO), 1833 (vs, CO), 1808 (br, s, CO).

$^1$H NMR (CD$_2$Cl$_2$): 7.01 (d, 2H, H$^3$, $^3$J$_{HH}$ = 8.8Hz), 7.3-7.7 (m, 13H, H 2,6, H 2',6', H 2'',6'', H 3',5', H3'',5'', H11, H11', H11''), 7.8-8.0 (m, 5H, H 9, H9', H10, H10', H10''), 8.2-8.3 (m, 1H, H 9''), 8.57-8.66 (m, 3H, H 7, H7', H12''), 8.73 (bs, 1H, H 7''), 9.38 (m, 2H, H12, H12').

4a: (Norbonadiene)Mo(CO)$_4$ (150 mg, 0.5 mmol) was added to a solution of 2a (293 mg, 0.5 mmol) in THF (40 mL). The solution turned dark purple. After stirring for 60 min (IR control) the volume of the solution was reduced to ca. 10 ml and diethyl ether was added giving a dark precipitate and a purple solution containing mononuclear complexes. The dark complex was repeatedly washed with diethyl ether until the ether remained colourless and dried in vacuo giving a black powder (349 mg, 88%).

Calcd for C$_{32}$H$_{19}$N$_5$O$_8$Mo$_2$ (793.4) C: 48.44, H: 2.41, N:8.83; found C: 48.17, H: 3.55, N: 8.47.

Osmometry (THF): M = 815g mol$^{-1}$.

MS (FAB): m/z = 792 (5, M$^+$-H), 380 (100, M$^+$-CN-(N∩N')-Mo-4CO).
UV/Vis (THF): $\lambda_{\text{max}} (\varepsilon) = 536 (5575)$, 600 (sh, 4545).
IR (THF): 2078 (m, CN), 2012 (m, CO), 1917 (vs, CO), 1904 (vs, CO), 1848 (vs, CO), 1824 (s, CO).
IR (CsI): 3340 (br, OH), 2088 (m, CN), 2013 (m, CO), 1913 (vs, CO), 1908 (vs, CO), 1833 (br, s, CO).

\[
\begin{align*}
\text{UV/Vis (THF): } & \lambda_{\text{max}} (\varepsilon) = 535 (15000), 600 (\text{sh, 13050}). \\
\text{IR (THF): } & 2070 \text{ (m, CN)}, 2013 \text{ (m, CO)}, 1918 \text{ (vs, CO)}, 1907 \text{ (sh, CO)}, 1851 \text{ (s, CO)}, 1827 \text{ (s, CO)}. \\
\text{IR (CsI): } & 3391 \text{ (br, OH)}, 2086 \text{ (m, CN)}, 2015 \text{ (m, CO)}, 1911 \text{ (br, vs, CO)}, 1832 \text{ (br, s, CO)}. \\
\end{align*}
\]

$^1$H NMR (CD$_2$Cl$_2$): 6.99 (d, 2H, $H^3$, $H^5$, $^3J_{HH} = 8.8$Hz), 7.3-7.8 (m, 8H, $H^2$, $H^6$, $H^{2',6'}$, $H^{3',5'}$, $H^{11}$, $H^{11'}$), 7.8-8.1 (m, 4H, $H^9$, $H^{9'}$, $H^{10}$, $H^{10'}$), 8.57 (s, 1H, $H^7$), 8.61 (s, 1H, $H^7$), 9.20 (d, 1H, $H^{12}$, $^3J_{HH} = 4.8$Hz), 9.30 (d, 1H, $H^{12}$, $^3J_{HH} = 4.8$Hz).

5a: (Norbonadiene)Mo(CO)$_4$ (60 mg, 0.2 mmol) was added to a solution of 3a (195 mg, 0.2 mmol) in THF (30 mL). After stirring for 3 h (IR control) the volume of the solution was reduced to ca. 8 ml and diethyl ether was added giving a dark precipitate and a purple solution containing mononuclear complexes. The dark complex was repeatedly washed with diethyl ether until the ether remained colourless. The residue was redissolved in THF, precipitated by adding diethyl ether and dried in vacuo giving a black powder (163 mg, 69%).


Osmometry (THF): $M = 1150$ g mol$^{-1}$.

UV/Vis (THF): $\lambda_{\text{max}} (\varepsilon) = 535 (15000)$, 600 (sh, 13050).

IR (THF): 2070 (m, CN), 2013 (m, CO), 1918 (vs, CO), 1907 (sh, CO), 1851 (s, CO), 1827 (s, CO).

IR (CsI): 3391 (br, OH), 2086 (m, CN), 2015 (m, CO), 1911 (br, vs, CO), 1832 (br, s, CO).

$^1$H NMR (CD$_2$Cl$_2$): 6.99 (d, 2H, $H^3$, $H^5$, $^3J_{HH} = 8.8$Hz), 7.3-8.7 (m, 13H, $H^2$, $H^6$, $H^{2',6'}$, $H^{3',5'}$, $H^{11}$, $H^{11'}$), 7.8-8.1 (m, 6H, $H^9$, $H^{9'}$, $H^{10}$, $H^{10'}$), 8.57 (s, 1H, $H^7$), 8.61 (s, 2H, $H^7$), 9.20 (d, 1H, $H^{12}$, $^3J_{HH} = 5.0$Hz), 9.29 (d, 2H, $H^{12}$, $^3J_{HH} = 4.8$Hz).
IR spectra of 4a and 5a (in THF) and their simulated spectra

Simulated IR spectrum of 4a:
addition of IR spectra of 2a (1×) + HO-(N∩N’)Mo(CO)₄ (1×)

Simulated IR spectrum of 5a:
addition of IR spectra of 2a (2×) + HO-(N∩N’)Mo(CO)₄ (1×)
UV/Vis spectra of 4a and 5a (in THF) and their simulated spectra

Simulated UV/Vis spectrum of 4a:
addition of UV/Vis spectra of 2a (1×) + HO-(N∩N’)Mo(CO)₄ (1×)

Simulated UV/Vis spectrum of 5a:
addition of UV/Vis spectra of 2a (2×) + HO-(N∩N’)Mo(CO)₄ (1×)