

**Table S1** Proton, and  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectroscopic data for  $[\text{MX}(\text{CO})(\eta\text{-RC}\equiv\text{CR})\text{Tp}]^+$  **1-18**,<sup>a</sup> NEW

Complex	$^1\text{H}$	$^{13}\text{C}$ - $\{^1\text{H}\}$
$[\text{MoF}(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}]^+$ <b>1</b>	1.45, 1.84, 2.33, 2.38, 2.45, 2.60 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.71, 3.35 (3H, s, $\text{MeC}\equiv\text{CMe}$ ), 5.68, 5.84, 5.89 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ).	12.6, 12.7, 13.2, 13.4, 14.8, 15.4 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 18.1, 20.7 (s, $\text{MeC}\equiv\text{CMe}$ ), 106.9, 107.1, 107.3 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 144.2, 144.7, 146.2, 149.6, 150.7, 152.4 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 197.3, 206.0 (s, $\text{MeC}\equiv\text{CMe}$ ), 237.3 (s, CO).
$[\text{MoCl}(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}]^+$ <b>2</b>	1.37, 2.02, 2.34, 2.40, 2.51, 2.58 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.80, 3.33 (3H, s, $\text{MeC}\equiv\text{CMe}$ ), 5.70, 5.84, 5.98 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ).	12.8, 12.9, 13.0, 15.3, 15.5, 15.7 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 19.3, 21.5 (s, $\text{MeC}\equiv\text{CMe}$ ), 107.3, 107.5, 107.8 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 144.4, 144.9, 146.1, 149.0, 152.1, 153.9 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 203.9, 213.8 (s, $\text{MeC}\equiv\text{CMe}$ ), 235.1 (s, CO).
$[\text{MoBr}(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}]^+$ <b>3</b>	1.32, 2.07, 2.34, 2.41, 2.51, 2.53 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.83, 3.29 (3H, s, $\text{MeC}\equiv\text{CMe}$ ), 5.69, 5.83, 6.01 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ).	12.8, 12.9, 13.0, 15.4, 16.4, 16.5 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 19.8, 21.9 (s, $\text{MeC}\equiv\text{CMe}$ ), 107.3, 107.7, 108.0 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 144.5, 145.1, 146.0, 148.7, 152.5, 154.3 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 205.3, 216.0 (s, $\text{MeC}\equiv\text{CMe}$ ), 235.1 (s, CO).
$[\text{MoI}(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}]^+$ <b>4</b>	1.28, 2.14, 2.34, 2.39, 2.41, 2.56 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.85, 3.24 (3H, s, $\text{MeC}\equiv\text{CMe}$ ), 5.68, 5.82, 6.05 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ).	13.0, 13.1, 15.2, 18.2, 18.7 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 20.3, 22.5 (s, $\text{MeC}\equiv\text{CMe}$ ), 107.2, 107.9, 108.2 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 144.7, 145.4, 145.8, 148.4, 153.0, 154.8 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 206.3, 218.5 (s, $\text{MeC}\equiv\text{CMe}$ ), 235.7 (s, CO).
$[\text{Mo}(\text{NCS})(\text{CO})(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}]^+$ <b>5</b>	1.36, 1.94, 2.35, 2.42, 2.50, 2.62 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 2.75, 3.38 (3H, s, $\text{MeC}\equiv\text{CMe}$ ), 5.73, 5.88, 5.97 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ).	12.8, 12.9, 13.0, 14.4, 15.1, 15.3 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 19.5, 21.9 (s, $\text{MeC}\equiv\text{CMe}$ ), 107.5, 107.6, 107.7 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 144.8, 145.5, 146.43, 149.1, 151.6, 153.5 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 206.5, 216.5 (s, $\text{MeC}\equiv\text{CMe}$ ), 232.5 (s, CO).
$[\text{MoF}(\text{CO})(\eta\text{-PhC}\equiv\text{CPh})\text{Tp}]^+$ <b>6</b>	1.26, 1.45, 2.38, 2.50, 2.53, 2.84 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 5.61, 5.78, 5.90 (3H, s,	12.6, 12.7, 13.2, 14.9, 15.0, 15.6 (s, $\text{C}_3\text{N}_2\text{HMe}_2$ ), 107.1, 107.4, 107.5 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$ ), 128.5, 128.6, 129.2, 129.3,

	<p><math>C_3N_2HMe_2</math>), 6.64-6.70 (2H, m, <i>PhC≡CPh</i>), 7.12-7.24, 7.49-7.65 (3H, m, <i>PhC≡CPh</i>), 7.86-7.92 (2H, m, <i>PhC≡CPh</i>).</p>	<p>130.1, 130.6, 135.5, 137.5 (s, <i>PhC≡CPh</i>), 144.2, 144.9, 146.8, 149.6, 151.3, 152.6 (s, 3,5-<math>C_3N_2HMe_2</math>), 198.8, 204.9 (s, <i>PhC≡CPh</i>), 238.7 (s, CO).</p>
[MoCl(CO)(η-PhC≡CPh)Tp] <sup>7</sup>	<p>1.26, 1.35, 2.37, 2.41, 2.57, 2.91 (3H, s, <math>C_3N_2HMe_2</math>), 5.69, 5.79, 5.89 (3H, s, <math>C_3N_2HMe_2</math>), 6.68-6.75 (2H, m, <i>PhC≡CPh</i>), 7.13-7.29, 7.54-7.69 (3H, m, <i>PhC≡CPh</i>), 8.04-8.10 (2H, m, <i>PhC≡CPh</i>).</p>	<p>12.9, 13.0, 13.1, 14.3, 15.6, 16.0 (s, <math>C_3N_2HMe_2</math>), 107.5, 107.7, 108.1 (s, 4-<math>C_3N_2HMe_2</math>), 128.7, 128.7, 129.3, 129.9, 130.1, 130.7, 135.8, 137.9 (s, <i>PhC≡CPh</i>), 144.5, 145.2, 146.7, 149.1, 152.6, 154.0 (s, 3,5-<math>C_3N_2HMe_2</math>), 203.3, 209.2 (s, <i>PhC≡CPh</i>), 236.4 (s, CO).</p>
[MoBr(CO)(η-PhC≡CPh)Tp] <sup>8</sup>	<p>1.34, 1.38, 2.41, 2.57, 2.59, 2.93 (3H, s, <math>C_3N_2HMe_2</math>), 5.72, 5.77, 5.89 (3H, s, <math>C_3N_2HMe_2</math>), 6.71-6.77 (2H, m, <i>PhC≡CPh</i>), 7.13-7.21 (2H, m, <i>PhC≡CPh</i>), 7.24-7.31 (1H, m, <i>PhC≡CPh</i>), 7.56-7.70 (3H, m, <i>PhC≡CPh</i>), 8.13-8.18 (2H, m, <i>PhC≡CPh</i>).</p>	<p>12.9, 13.0, 13.1, 15.4, 15.5, 16.8 (s, <math>C_3N_2HMe_2</math>), 107.4, 107.8, 108.2 (s, 4-<math>C_3N_2HMe_2</math>), 128.5, 128.7, 129.3, 129.9, 130.0, 130.8, 135.9, 137.9 (s, <i>PhC≡CPh</i>), 144.6, 145.3, 146.6, 148.9, 153.0, 154.3 (s, 3,5-<math>C_3N_2HMe_2</math>), 203.9, 210.9 (s, <i>PhC≡CPh</i>), 236.1 (s, CO).</p>
[MoI(CO)(η-PhC≡CPh)Tp] <sup>9</sup>	<p>1.30, 1.43, 2.40, 2.57, 2.62, 2.94 (3H, s, <math>C_3N_2HMe_2</math>), 5.76, 5.77, 5.88 (3H, s, <math>C_3N_2HMe_2</math>), 6.73-6.78 (2H, s, <i>PhC≡CPh</i>), 7.13-7.21 (2H, m, <i>PhC≡CPh</i>), 7.27-7.34 (1H, m, <i>PhC≡CPh</i>), 7.58-7.69 (3H, s, <i>PhC≡CPh</i>), 8.23-8.29 (2H, s, <i>PhC≡CPh</i>).</p>	<p>13.0, 13.1, 13.2, 15.5, 17.6, 18.5 (s, <math>C_3N_2HMe_2</math>), 107.4, 108.1, 108.5 (s, 4-<math>C_3N_2HMe_2</math>), 128.4, 128.9, 129.4, 130.1, 130.2, 131.2, 136.4, 137.9 (s, <i>PhC≡CPh</i>), 144.8, 145.5, 146.5, 149.0, 153.6, 154.7 (s, 3,5-<math>C_3N_2HMe_2</math>), 204.5, 213.6 (s, <i>PhC≡CPh</i>), 236.4 (s, CO).</p>
[WF(CO)(η-MeC≡CMe)Tp] <sup>10</sup>	<p>1.51, 2.03, 2.33, 2.39, 2.47, 2.66 (3H, s, <math>C_3N_2HMe_2</math>), 2.84, 3.37 (3H, s, <i>MeC≡CMe</i>), 5.70, 5.86, 5.97 (3H, s, <math>C_3N_2HMe_2</math>).</p>	<p>12.6, 12.7, 13.0, 13.5, 14.8, 16.3 (s, <math>C_3N_2HMe_2</math>), 17.8, 20.4 (s, <i>MeC≡CMe</i>), 107.2, 107.3, 107.5 (s, 4-<math>C_3N_2HMe_2</math>), 144.2, 144.9, 146.2, 151.0, 151.5, 152.9 (s, 3,5-<math>C_3N_2HMe_2</math>), 193.5, 200.2 (s, <i>MeC≡CMe</i>), 240.8 (s, CO).</p>
[WCl(CO)(η-MeC≡CMe)Tp] <sup>11</sup>	<p>1.47, 2.21, 2.33, 2.41, 2.51, 2.78 (3H, s, <math>C_3N_2HMe_2</math>), 2.79, 3.34 (3H, s, <i>MeC≡CMe</i>),</p>	<p>12.8, 12.9, 15.7, 16.0, 16.5 (s, <math>C_3N_2HMe_2</math>), 19.0, 21.2 (s, <i>MeC≡CMe</i>), 107.3, 107.8, 108.2 (s, 4-<math>C_3N_2HMe_2</math>), 144.3,</p>

	5.70, 5.86, 6.06 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ).	145.2, 146.0, 150.6, 153.2, 154.5 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 199.5, 208.1 (s, MeC≡CMe), 235.4 (s, CO).
[WBr(CO)(η-MeC≡CMe)Tp] <sup>+</sup> <b>12</b>	1.44, 2.27, 2.34, 2.42, 2.53, 2.73 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.81, 3.32 (3H, s, MeC≡CMe), 5.70, 5.86, 6.08 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ).	12.8, 12.9, 16.5, 16.8 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 19.5, 21.5 (s, MeC≡CMe), 107.3, 108.0, 108.3 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 144.4, 145.3, 146.0, 150.4, 153.7, 155.0 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 201.2, 210.0 (s, MeC≡CMe).
[W(NCS)(CO)(η-MeC≡CMe)Tp] <sup>+</sup> <b>14</b>	1.46, 1.53, 2.14, 2.34, 2.50, 2.72 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 2.82, 3.39 (3H, s, MeC≡CMe), 5.74, 5.90, 6.05 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ).	11.6, 12.8, 12.9, 14.8, 15.4, 16.3 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 19.2, 21.5 (s, MeC≡CMe), 107.5, 107.9, 108.0 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 144.7, 145.7, 146.4, 146.4, 152.6, 153.9 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 205.9, 213.6 (s, MeC≡CMe), 234.1 (s, CO).
[WF(CO)(η-PhC≡CPh)Tp] <sup>+</sup> <b>15</b>	1.42, 1.53, 2.39, 2.51, 2.54, 2.80 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.72, 5.77, 5.92 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.59-6.67 (m, 2H, <i>o</i> -PhC <sub>2</sub> Ph), 7.12-7.23 (m, 3H, <i>m</i> - and <i>p</i> -PhC <sub>2</sub> Ph), 7.44-7.54 (m, 1H, <i>p</i> -PhC <sub>2</sub> Ph), 7.54-7.65 (m, 2H, <i>m</i> -PhC <sub>2</sub> Ph), 7.77-7.85 (m, 2H, <i>o</i> -PhC <sub>2</sub> Ph).	11.5, 11.9, 15.4 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 106.3, 106.4, 106.7 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 127.4, 127.7, 128.0, 128.1, 129.8, 135.2, 137.5 (s, PhC≡CPh), 143.1, 144.1, 145.7, 149.9, 150.9, 151.9 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 195.6, 201.5 (s, PhC≡CPh), 241.6 (s, CO).
[WCl(CO)(η-PhC≡CPh)Tp] <sup>+</sup> <b>16</b>	1.43, 1.46, 2.32, 2.48, 2.50, 2.82 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.70, 5.71, 5.84 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.54-6.60 (m, 2H, <i>o</i> -PhC <sub>2</sub> Ph), 7.08-7.13 (m, 3H, <i>m</i> - and <i>p</i> -PhC <sub>2</sub> Ph), 7.40-7.49 (m, 1H, <i>p</i> -PhC <sub>2</sub> Ph), 7.50-7.59 (m, 2H, <i>m</i> -PhC <sub>2</sub> Ph), 7.80-7.87 (m, 2H, <i>o</i> -PhC <sub>2</sub> Ph).	12.8, 12.9, 14.7, 16.2, 16.7 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 107.4, 108.0, 108.5 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 128.5, 129.2, 129.3, 129.4, 130.1, 130.5, 136.8, 138.9 (s, PhC≡CPh), 144.3, 145.5, 146.6, 150.7, 153.7, 154.7 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 200.6, 206.7 (s, PhC≡CPh), 237.0 (s, CO).
[WBr(CO)(η-PhC≡CPh)Tp] <sup>+</sup> <b>17</b>	1.41, 1.50, 2.31, 2.50, 2.52, 2.84 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.70, 5.74, 5.83 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.54-6.61 (m, 2H, <i>o</i> -PhC <sub>2</sub> Ph), 7.04-7.19 (m, 3H, <i>m</i> - and <i>p</i> -PhC <sub>2</sub> Ph), 7.42-	11.7, 11.8, 14.7, 15.6, 15.9 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 106.2, 107.1, 107.5 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 127.6, 128.1, 128.4, 129.2, 129.3, 135.9, 137.9 (s, PhC≡CPh), 143.3, 144.5, 145.5, 149.5, 153.2, 154.1 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 200.3, 207.2 (s,

	7.49 (m, 1H, <i>p-PhC<sub>2</sub>Ph</i> ), 7.51-7.60 (m, 2H, <i>m-PhC<sub>2</sub>Ph</i> ), 7.86-7.94 (m, 2H, <i>o-PhC<sub>2</sub>Ph</i> ).	PhC≡CPh), 235.8 (s, CO).
[WI(CO)(η-PhC≡CPh)Tp] <sup>a</sup> <b>18</b>	1.38, 2.31, 2.32, 2.50, 2.54, 2.86 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 5.69, 5.78, 5.83 (3H, s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 6.55-6.62 (m, 2H, <i>o-PhC<sub>2</sub>Ph</i> ), 7.05-7.21 (m, 3H, <i>m</i> - and <i>p-PhC<sub>2</sub>Ph</i> ), 7.05-7.21 (m, 3H, <i>m</i> - and <i>p-PhC<sub>2</sub>Ph</i> ), 7.96-8.03 (m, 2H, <i>o-PhC<sub>2</sub>Ph</i> ).	11.7, 11.9, 15.5, 16.0, 17.7 (s, C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 106.1, 107.3, 107.6 (s, 4-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 127.7, 127.9, 128.1, 128.4, 129.3, 129.4, 136.1, 137.70 (s, PhC≡CPh), 143.4, 144.7, 145.1, 149.4, 153.9, 154.4 (s, 3,5-C <sub>3</sub> N <sub>2</sub> HMe <sub>2</sub> ), 201.0, 209.8 (s, PhC≡CPh), 234.0 (s, CO).

<sup>a</sup> Chemical shift (δ) in ppm, *J* values in Hz, spectra in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.