

Supplementary data. Proton, ^{13}C - $\{^1\text{H}\}$ and ^{31}P NMR spectroscopic data for alkyne complexes.^a

Complex	^1H	^{13}C - $\{^1\text{H}\}$	^{31}P
$[\text{Mo}(\text{CO})_2(\eta\text{-PhC}\equiv\text{CPh})\text{Tp}'][\text{PF}_6]$ $\mathbf{1}^+[\text{PF}_6]^-$	1.12 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.52 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.66 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.82 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 5.87 (s, 2H, $\text{C}_3\text{N}_2\text{HMe}_2$), 6.15 (s, 1H, $\text{C}_3\text{N}_2\text{HMe}_2$), 7.15-8.36 (m, 10H, Ph).	13.0, 13.4, 14.8, 16.4 (s, $\text{C}_3\text{N}_2\text{HMe}_2$), 108.7, 109.8 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$), 128.4, 128.8, 130.0, 130.3, 130.9, 131.2, 131.3, 131.4, 134.7, 136.8 (s, $\text{PhC}\equiv\text{CPh}$), 147.9, 150.3, 150.5, 154.9 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$), 207.0, 231.4 ($\text{PhC}\equiv\text{CPh}$), 219.3 (s, CO).	-
$[\text{Mo}(\text{CO})_2(\eta\text{-4-MeO}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-4})\text{Tp}'][\text{PF}_6]$ $\mathbf{2}^+[\text{PF}_6]^-$ ^b	1.11 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.52 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.65 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.81 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 3.88 (s, 3H, $\text{C}_6\text{H}_4\text{OMe-4}$), 4.05 (s, 3H, $\text{C}_6\text{H}_4\text{OMe-4}$), 5.86 (s, 2H, $\text{C}_3\text{N}_2\text{HMe}_2$), 6.12 (s, 1H, $\text{C}_3\text{N}_2\text{HMe}_2$), 6.87 (d, 2H, J 8, $\text{C}_6\text{H}_4\text{OMe-4}$), 7.18 (d, 2H, J 8, $\text{C}_6\text{H}_4\text{OMe-4}$), 7.39 (d, 2H, J 8, $\text{C}_6\text{H}_4\text{OMe-4}$), 8.45 (d, 2H, J 8, $\text{C}_6\text{H}_4\text{OMe-4}$).	13.0, 13.4, 14.6, 16.3 (s, $\text{C}_3\text{N}_2\text{HMe}_2$), 56.5, 56.6 ($\text{C}_6\text{H}_4\text{OMe-4}$), 108.5, 109.4 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$), 115.3, 116.1, 129.04, 129.77, 134.6, 134.9, 165.1, 166.1 ($\text{C}_6\text{H}_4\text{OMe-4}$), 147.4, 149.7, 150.5, 154.6 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$), 204.9, 228.2 ($\text{PhC}\equiv\text{CPh}$), 220.4 (s, CO).	-
$[\text{Mo}(\text{CO})_2(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}'][\text{PF}_6]$ $\mathbf{3}^+[\text{PF}_6]^-$	1.36 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.46 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.59 (s, 6H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.64 (s, 3H, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.78 (br.s., 3H, $\text{MeC}\equiv\text{CMe}$), 3.65	13.1, 13.5, 15.1, 16.0 (s, $\text{C}_3\text{N}_2\text{HMe}_2$), 24.2, 24.9 (s, $\text{MeC}\equiv\text{CMe}$), 108.2, 109.5 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$), 147.3, 149.5, 150.0, 154.9 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$), 210.6, 242.4 ($\text{MeC}\equiv\text{CMe}$), 219.4 (s, CO).	-

	(br.s., 3H, <i>MeC≡CMe</i>), 5.98 (s, 2H, <i>C₃N₂HMe₂</i>), 6.07 (s, 1H, <i>C₃N₂HMe₂</i>).		
[Mo(CO) ₂ (η- <i>PhC≡CH</i>)Tp'] ₂ [PF ₆] 4 ⁺ [PF ₆] ⁻	1.07 (s, 6H, <i>C₃N₂HMe₂</i>), 2.47 (s, 3H, <i>C₃N₂HMe₂</i>), 2.62 (s, 6H, <i>C₃N₂HMe₂</i>), 2.70 (s, 3H, <i>C₃N₂HMe₂</i>), 5.84 (s, 2H, <i>C₃N₂HMe₂</i>), 6.08 (s, 1H, <i>C₃N₂HMe₂</i>), 7.20 (m, 2H, Ph), 7.36 (m, 2H, Ph), 7.59 (m, 1H, Ph), 13.08 (s, 1H, <i>C≡CH</i>).	13.0, 13.5, 14.8, 16.1 (s, <i>C₃N₂HMe₂</i>), 108.5, 109.8 (s, 4- <i>C₃N₂HMe₂</i>), 128.8, 130.1, 130.7, 134.1 (s, <i>PhC≡CPh</i>), 147.7, 148.2, 150.2, 152.5 (s, 3,5- <i>C₃N₂HMe₂</i>), 201.6 (s, <i>≡CH</i>), 217.7 (s, CO), 225.2 (s, <i>≡CPh</i>).	-
[Mo(CO)(NCMe)(η- <i>MeC≡CMe</i>)Tp'] ₂ [PF ₆] 8 ⁺ [PF ₆] ⁻	1.24 (s, 3H, <i>C₃N₂HMe₂</i>), 1.85 (3H, s, <i>NCMe</i>), 2.42 (s, 3H, <i>C₃N₂HMe₂</i>), 2.47 (s, 3H, <i>C₃N₂HMe₂</i>), 2.50 (3H, s, <i>C₃N₂HMe₂</i>), 2.54 (s, 3H, <i>C₃N₂HMe₂</i>), 2.61 (s, 3H, <i>C₃N₂HMe₂</i>), 2.78, 3.62 (s, 3H, <i>MeC≡CMe</i>), 5.79, 5.99, 6.05 (s, 1H, <i>C₃N₂HMe₂</i>).	4.8 (<i>NCMe</i>), 12.8, 13.0, 13.1, 14.5, 15.2, 15.4 (s, <i>C₃N₂HMe₂</i>), 21.6, 23.5 (s, <i>MeC≡CMe</i>), 108.0, 108.2, 108.3 (s, 4- <i>C₃N₂HMe₂</i>), 145.9, 147.3, 147.7, 149.0, 151.5, 153.5 (s, 3,5- <i>C₃N₂HMe₂</i>), 148.8 <i>NCMe</i> , 218.9, 231.4 (<i>MeC≡CMe</i>), 228.3 (s, CO).	-
[W(CO){P(OCH ₂) ₃ CEt}(η- <i>MeC≡CMe</i>)Tp'] ₂ [BF ₄] 10 ⁺ [BF ₄] ⁻	0.81 {t, 3H, <i>J</i> 8, P(OCH ₂) ₃ CEt}, 1.25 {q, 2H, <i>J</i> 8, P(OCH ₂) ₃ CEt}, 1.30, 2.05, 2.39, 2.48, 2.58, 2.67 (3H, s, <i>C₃N₂HMe₂</i>), 2.83, 3.46 (3H, s, <i>MeC≡CMe</i>), 4.24 {d, 6H, ³ <i>J</i> _{P,H} 5, P(OCH ₂) ₃ CEt}, 5.81, 6.01, 6.16 (1H, s, <i>C₃N₂HMe₂</i>).	7.2 {s, P(OCH ₂) ₃ CEt}, 12.6, 13.0, 13.5, 15.7, 15.9, 16.1 (s, <i>C₃N₂HMe₂</i>), 22.3, 36.0 (s, <i>MeC≡CMe</i>), 75.8 {d, <i>J</i> _{P,C} 6, P(OCH ₂) ₃ CEt}, 107.9, 109.2, 109.9 (s, 4- <i>C₃N₂HMe₂</i>), 146.3, 146.8, 149.3, 149.9, 154.3, 156.9 (s, 3,5- <i>C₃N₂HMe₂</i>), 212.6 (d,	131.9 {d, <i>J</i> _{W,P} 494, P(OCH ₂) ₃ CEt}.

		$J_{\text{P,C}}$ 10, $\text{MeC}\equiv\text{CMe}$), 223.4 (d, $J_{\text{P,C}}$ 7, $\text{MeC}\equiv\text{CMe}$), 236.9 (s, CO).	
$[\text{Mo}(\text{CO})\{\text{P}(\text{OCH}_2)_3\text{CEt}\}(\eta\text{-MeC}\equiv\text{CMe})\text{Tp}'][\text{PF}_6]\mathbf{11}^+[\text{PF}_6]^-$	0.81 {t, 3H, J 8, $\text{P}(\text{OCH}_2)_3\text{CEt}$ }, 1.26 {q, 2H, J 8, $\text{P}(\text{OCH}_2)_3\text{CEt}$ }, 1.14, 1.82, 2.42, 2.48, 2.59, 2.67 (3H, s, $\text{C}_3\text{N}_2\text{HMe}_2$), 2.75, 3.51 (3H, s, $\text{MeC}\equiv\text{CMe}$), 4.25 {d, 6H, $^3J_{\text{P,H}}$ 5, $\text{P}(\text{OCH}_2)_3\text{CEt}$ }, 5.77, 5.98, 6.10 (1H, s, $\text{C}_3\text{N}_2\text{HMe}_2$).	7.1, 7.6 {s, $\text{P}(\text{OCH}_2)_3\text{CEt}$ }, 12.7, 13.1, 13.5, 14.7, 15.3, 15.4 (s, $\text{C}_3\text{N}_2\text{HMe}_2$), 23.6, 36.1 (s, $\text{MeC}\equiv\text{CMe}$), 75.4 {d, $J_{\text{P,C}}$ 5, $\text{P}(\text{OCH}_2)_3\text{CEt}$ }, 107.7, 108.9, 109.3 (s, 4- $\text{C}_3\text{N}_2\text{HMe}_2$), 146.4, 146.8, 148.3, 148.8, 152.7, 155.9 (s, 3,5- $\text{C}_3\text{N}_2\text{HMe}_2$), 218.6 (d, $J_{\text{P,C}}$ 11, $\text{MeC}\equiv\text{CMe}$), 227.5 (d, $J_{\text{P,C}}$ 14, $\text{MeC}\equiv\text{CMe}$), 244.4 (s, CO).	139.5 {s, $\text{P}(\text{OCH}_2)_3\text{CEt}$ },

^a Chemical shift (δ) in ppm, J values in Hz, spectra in CD_2Cl_2 at 20 °C unless stated otherwise. ^b At –40 °C.

