

## Supplementary Information

### A radical pathway to synthesise Mo and W dithiolene complexes

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#### Experimental

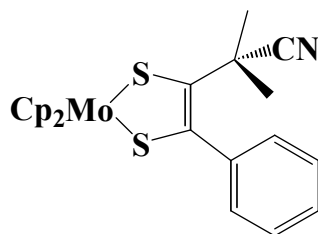
Reagents were obtained from commercial sources (Sigma Aldrich Company Ltd.; Lancaster Synthesis Ltd.; and Fischer Scientific) and used without further purification. Dry toluene was prepared by passing the solvent down an activated alumina column under a nitrogen atmosphere.  $[\text{Cp}_2\text{M}(\text{S}_4)]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) was synthesised from  $[\text{Cp}_2\text{MCl}_2]$  (Sigma Aldrich Company Ltd.).<sup>1</sup> 2-Ethynylquinoxaline was synthesised by the method of Dinsmore.<sup>2</sup> All reactions were carried out under an argon atmosphere using standard Schlenk-line techniques, unless stated to the contrary.

Elemental analyses were performed either in the Microanalytical Laboratories at the University of Nottingham or the Science Centre at London Metropolitan University.

The mass spectrometry measurements were performed using Electrospray ionisation (ESI) for samples in MeCN:water (1:1, v/v) solution on a Bruker MicroTof spectrometer.

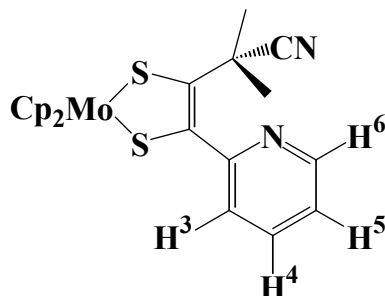
$^1\text{H}$  NMR spectra were recorded on a Bruker DPX300 spectrometer.

#### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$



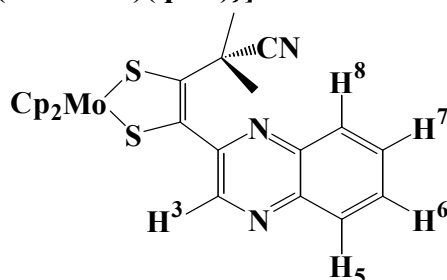
AIBN (138 mg, 0.84 mmol) was dissolved in anhydrous toluene (10 cm<sup>3</sup>), phenylacetylene (0.1 cm<sup>3</sup>, 0.8 mmol) was added and the mixture stirred under an Ar atmosphere at 70 °C. A solution of  $[\text{Cp}_2\text{Mo}(\text{S}_4)]$  (100 mg, 0.28 mmol) in anhydrous DMF (2 cm<sup>3</sup>) and anhydrous toluene (5 cm<sup>3</sup>) was added slowly (in three portions) to the reaction mixture that was then heated at 90 °C for 5 h. After this time, the solvent was removed under a reduced pressure to produce a red compound. Column chromatography (silica gel 60, 220-440 mesh) of this solid in  $\text{CH}_2\text{Cl}_2$  gave, on elution with  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$  (98:2) to give the product as a single red band that was collected and evaporated to dryness; a red solid was obtained. Yield 25 mg, 20% (Found: C, 57.75; H, 4.58; N, 2.74 %. Calc. for  $\text{C}_{22}\text{H}_{21}\text{NMoS}_2$ : C, 57.51; H, 4.61, N, 3.05 %).  $^1\text{H}$  NMR {300 MHz,  $\text{CDCl}_3$ }:  $\delta$  /ppm 7.15 - 7.31 (m, 5H,  $\text{C}_6\text{H}_5$ ), 5.33 (s, 10H,  $2\times\text{Cp}$ ), 1.50 (s, 6H,  $2\times\text{CH}_3$ ). IR Spectrum ( $\text{cm}^{-1}$ ): (KBr disc) 3108 (m), 2228 (m), 1600 (m), 1440 (m), 1223 (m), 1071 (s), 831 (s). Mass Spectrum (+ESI):  $m/z$  460  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{Me}_2\text{CN})(\text{Ph})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(2\text{-py})\}]$



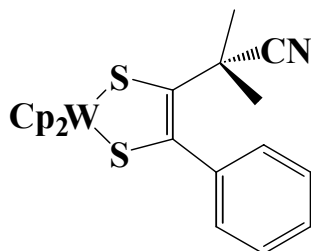
This preparation was accomplished in a manner similar to that described for  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$  except that 2-ethynylpyridine (0.1 cm<sup>3</sup>, 0.8 mmol) was used in place of phenylacetylene. Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH<sub>2</sub>Cl<sub>2</sub> gave, on elution with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (98:2) to give the product as a single green band that was collected and evaporated to dryness; a purple solid was obtained. Yield 38 mg, 30% (Found: C, 55.13; H, 4.98; N, 6.47 %. Calc. for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>MoS<sub>2</sub>: C, 54.78; H, 4.38, N, 6.08 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 8.56 (d, [J<sub>H-H</sub> = 3.7 Hz], H<sup>6</sup>), 7.62 (t, [J<sub>H-H</sub> = 7.0 Hz], H<sup>4</sup>), 7.34 (d, [J<sub>H-H</sub> = 7.7 Hz], H<sup>3</sup>), 7.13 (t, [J<sub>H-H</sub> = 7.1 Hz], H<sup>5</sup>), 5.30 (s, 10H, 2×Cp), 1.61 (s, 6H, 2×CH<sub>3</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 3114 (m), 2223(m), 1582 (m), 1465 (m), 1260 (m), 1096 (s), 809 (s). Mass Spectrum (+ESI): *m/z* 463  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{Me}_2\text{CN})(2\text{-py})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{quin})\}]$



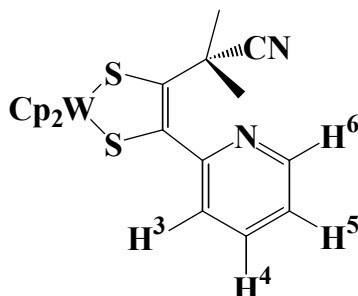
This preparation was accomplished in a manner similar to that described for  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$ , except that 2-ethynylquinoxaline<sup>34</sup> (45 mg, 0.28 mmol) was used in place of phenylacetylene. Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH<sub>2</sub>Cl<sub>2</sub> gave, on elution with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (98:2) to give the product as a single purple band that was collected and evaporated to dryness; a red solid was obtained. Yield 32mg, 25% (Found: C, 56.24; H, 4.24; N, 7.77 %. Calc. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>MoS<sub>2</sub>: C, 56.35; H, 4.14, N, 8.21 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 8.86 (s, H<sup>3</sup>), 8.04 (m, H<sup>5/8</sup>), 7.68 (d, H<sup>6/7</sup>), 5.32 (s, 10H, 2×Cp), 1.69 and 1.60 (s, 2×3H, 2×CH<sub>3</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 3114 (m), 2223 (m), 1588 (m), 1434 (m), 1265 (m), 1116 (s), 809 (s) Mass Spectrum (+ESI): *m/z* 511  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{quin})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$



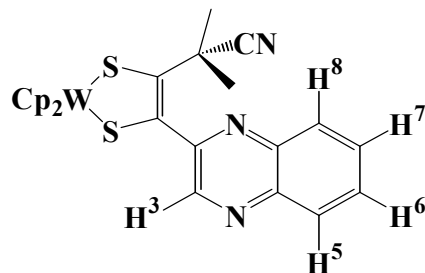
AIBN (100 mg, 0.66 mmol) was dissolved in anhydrous toluene (10 cm<sup>3</sup>), phenylacetylene (0.1 cm<sup>3</sup>, 0.8 mmol) was added and the mixture was stirred under an Ar atmosphere at 70 °C. A solution of  $[\text{Cp}_2\text{W}(\text{S}_4)]$  (60 mg, 0.14 mmol) in anhydrous DMF (2 cm<sup>3</sup>) and anhydrous toluene (5 cm<sup>3</sup>) was added slowly (in three portions) to the reaction mixture that was then heated at 90 °C for 5 h. After this time, the solvent was removed under a reduced pressure and an orange solid was obtained. Column chromatography (silica gel 60, 220-440 mesh) of the solid in CH<sub>2</sub>Cl<sub>2</sub> gave, on elution with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (98:2) to give the product as a single orange band that was collected and evaporated to dryness; an orange solid was obtained. Yield 15 mg, 20% (Found: C, 48.27; H, 3.96; N, 2.49 %. Calc. for C<sub>22</sub>H<sub>21</sub>NWS<sub>2</sub>: C, 48.27; H, 3.87, N, 2.56 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 7.09- 7.33 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 5.33 (s, 10H, 2×Cp), 1.57 (s, 6H, 2× CH<sub>3</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 3103 (m), 2229 (m), 1613 (m), 1436 (m), 1255 (m), 1092 (s), 829 (s). Mass Spectrum (+ESI): *m/z* 548  $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(2\text{-py})\}]$



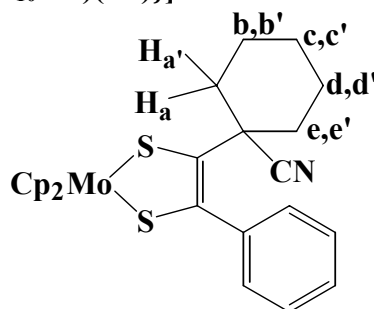
This preparation was accomplished in a manner similar to that for  $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$  except that 2-ethynylpyridine (0.1 cm<sup>3</sup>, 0.8 mmol). Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH<sub>2</sub>Cl<sub>2</sub> gave, on elution with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (98:2) to give the product as a single red band that was collected and evaporated to dryness; a red solid was obtained. Yield 15 mg, 20 % (Found: C, 46.10; H, 3.76; N, 4.98 %. Calc. for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>WS<sub>2</sub>: C, 46.00; H, 3.68; N, 5.11 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 8.56 (d, H<sup>6</sup>), 7.62 (t, H<sup>4</sup>), 7.32 (d, H<sup>3</sup>), 7.13 (t, H<sup>5</sup>), 5.29 (s, 10H, 2×Cp), 1.60 (s, 6H, 2× CH<sub>3</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 3110 (m), 2220 (m), 1570 (m), 1460 (m), 1260 (m), 1096 (s), 809 (s). Mass Spectrum (+ESI): *m/z* 549  $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(2\text{-py})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{quin})\}]$



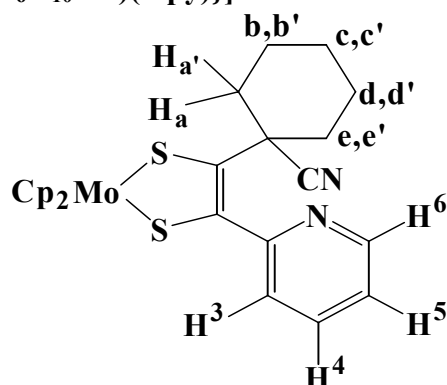
This preparation was similar to that of  $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{Ph})\}]$  except that 2-ethynylquinoxaline<sup>34</sup> (22 mg, 0.14 mmol) was used in place of phenylacetylene. Column chromatography (silica gel 60, 220-440 mesh) of the crude product in  $\text{CH}_2\text{Cl}_2$  gave, on elution with  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  (98:2) to give the product as a single purple band which was collected and evaporated to dryness; a red solid was obtained. Yield 17 mg, 20 % (Found: C, 47.99; H, 3.43; N, 6.91 %. Calc. for  $\text{C}_{24}\text{H}_{21}\text{N}_3\text{WS}_2$ : C, 48.09; H, 3.53; N, 7.01%).  $^1\text{H}$  NMR {300 MHz,  $\text{CDCl}_3$ }:  $\delta$  /ppm 8.85 (s, H<sup>3</sup>), 8.03 (m, H<sup>5/8</sup>), 7.68(d, H<sup>6/7</sup>), 5.29 (s, 10H, 2×Cp), 1.69 (s, 6H, 2×CH<sub>3</sub>). IR Spectrum ( $\text{cm}^{-1}$ ): (KBr disc) 3099 (m), 2225 (m), 1500 (m), 1382 (m), 1264 (m), 1116 (s), 838 (s). Mass Spectrum (+ESI):  $m/z$  599  $[\text{Cp}_2\text{W}\{\text{S}_2\text{C}_2(\text{CMe}_2\text{CN})(\text{quin})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_{10}\text{CN})(\text{Ph})\}]$



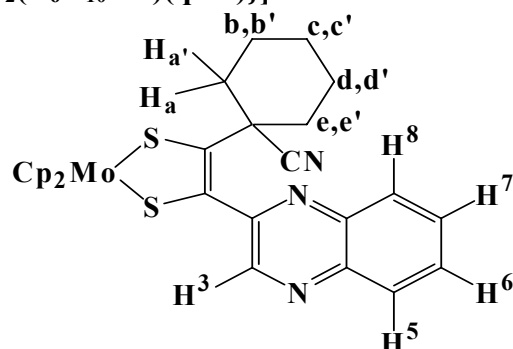
ACCN (220 mg, 0.90 mmol) and phenylacetylene (0.1 cm<sup>3</sup>, 0.90 mmol) were dissolved in dry toluene (20 cm<sup>3</sup>) and heated at 90 °C under argon for 20 mins.  $[\text{Cp}_2\text{Mo}(\text{S}_4)]$  (80 mg, 0.23 mmol) in anhydrous DMF (2 cm<sup>3</sup>) was added dropwise to the reaction mixture which was then heated to reflux at 100 °C for 8 h. After this time, the solvent was removed under a reduced pressure to give a brown-black solid. Column chromatography (silica gel 60, 220-440 mesh) of the solid gave, on elution with EtOAc and *n*-hexane (4:1), the product as a single red band which was collected and evaporated to dryness to give a dark red solid. Dark red crystals were obtained by solvent diffusion of *n*-hexane into a solution of  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_5\text{CN})\text{Ph}\}]$  in  $\text{CH}_2\text{Cl}_2$ . The solvent was removed by decantation and the product dried under a reduced pressure. Yield 57 mg, 50 % (Found: C, 60.18; H, 5.00; N, 2.60 %. Calc. for  $\text{C}_{25}\text{H}_{25}\text{MoS}_2\text{N}$ : C, 60.11; H, 5.04, N, 2.80 %).  $^1\text{H}$  NMR {300 MHz,  $\text{CDCl}_3$ }:  $\delta$  /ppm 7.21 - 7.42 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 5.32 (s, 10H, 2×Cp), 2.03 (m, 2H, H<sub>a,a'</sub>), 1.82 (m, 2H, H<sub>e,e'</sub>), 1.62 (m, 3H, H<sub>b,b',d</sub>), 1.30 (m, 1H, H<sub>d'</sub>), 1.09 (m, 1H, H<sub>c</sub>), 0.88 (m, 1H, H<sub>c</sub>). IR Spectrum ( $\text{cm}^{-1}$ ): (KBr disc) 2923 (m), 2228 (m), 1634 (m), 1381 (s), 1261 (m), 811(s). Mass Spectrum (+ESI):  $m/z$  501  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_{10}\text{CN})(\text{Ph})\}]^+$ .

### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_{10}\text{CN})(2\text{-py})\}]$



ACCN (270 mg, 1.10 mmol) and 2-ethynylpyridine (0.1 cm<sup>3</sup>, 0.90 mmol) were dissolved in dry toluene (20 cm<sup>3</sup>) and heated at 90 °C under argon for 20 mins.  $[\text{Cp}_2\text{Mo}(\text{S}_4)]$  (100 mg, 0.34 mmol) in anhydrous DMF (2 cm<sup>3</sup>) was added dropwise into the reaction mixture that was heated to reflux at 100 °C for 8 h. After this time, the solvent was removed under a reduced pressure to give a purple solid. Column chromatography (silica gel 60, 220-440 mesh) of this solid gave, on elution with EtOAc and *n*-hexane (4:1), the product as a single purple band which was collected and evaporated to dryness. The dark purple solid was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane was added until the product precipitated as a purple solid. The solvent was removed by decantation and the product dried under a reduced pressure. Yield 35 mg, 25 %. (Found: C, 57.58; H, 4.86; N, 5.51 %. Calc. for C<sub>24</sub>H<sub>24</sub>MoS<sub>2</sub>N<sub>2</sub>: C, 57.85; H, 4.83, N, 5.60 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 8.57 (d, [*J*<sub>H-H</sub> = 4.1 Hz], H<sup>6</sup>), 7.63 (td, [*J*<sub>1(H-H)}</sub> = 7.8 Hz, *J*<sub>2(H-H)}</sub> = 1.8 Hz ], H<sup>5</sup>), 7.35 (d, [*J*<sub>H-H</sub> = 7.5 Hz], H<sup>3</sup>), 7.14 (t, [*J*<sub>H-H</sub> = 5.9 Hz], H<sup>4</sup>), 5.30 (s, 10H, 2×Cp), 2.12 (m, 2H, H<sub>aa'</sub>), 1.96 (td, [*J*<sub>1(H-H)}</sub> = 11.9, *J*<sub>2(H-H)}</sub> = 5.9 Hz, 2H, H<sub>ee'</sub>), 1.62 (m, 3H, H<sub>bb'd</sub>), 1.28 (m, 1H, H<sub>d'</sub>), 1.08 (m, 1H, H<sub>c</sub>), 0.88 (m, 1H, H<sub>c'</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 2927 (m), 2217 (m), 1646 (b), 1460 (m), 1382 (s), 1259 (b), 809 (s). Mass Spectrum (+ESI): *m/z* 500  $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_{10}\text{CN})(2\text{-py})\}]^+$ .

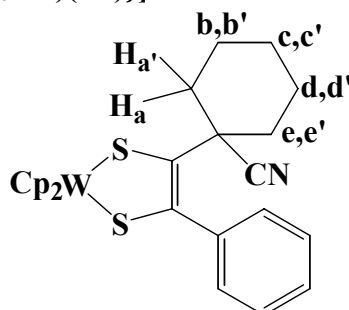
### Synthesis of $[\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_{10}\text{CN})(\text{quin})\}]$



ACCN (270 mg, 1.10 mmol) and 2-ethynylquinoxaline (100 mg, 0.7 mmol) were dissolved in dry toluene (20 cm<sup>3</sup>) and heated at 90 °C under argon for 20 mins.  $[\text{Cp}_2\text{Mo}(\text{S}_4)]$  (100 mg, 0.34 mmol) in anhydrous DMF (2 cm<sup>3</sup>) was added dropwise into the reaction mixture that was heated to reflux at 100 °C for 8 h. After this time, the solvent was removed under a

reduced pressure to give a purple solid. Column chromatography (silica gel 60, 220-440 mesh) of the solid gave, on elution with EtOAc and *n*-hexane (4:1), the product as a single purple-red band which was collected and evaporated to dryness. The purple-red solid was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane was added until the product precipitated as a dark red solid. The solvent was removed by decantation and the product dried under a reduced pressure. Yield 55 mg, 29 %. (Found: C, 58.89; H, 4.60; N, 7.59 %. Calc. for C<sub>27</sub>H<sub>24</sub>MoS<sub>2</sub>N<sub>3</sub>: C, 58.79; H, 4.57, N, 7.60 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 8.87 (s, H<sup>3</sup>), 8.06 (m, H<sup>5/8</sup>), 7.69 (m, H<sup>6/7</sup>), 5.34 (s, 10H, 2×Cp), 2.26 (m, 2H, H<sub>a,a'</sub>), 2.06 (td, [*J*<sub>1(H-H)</sub> = 11.4, *J*<sub>2(H-H)</sub> = 5.4 Hz], 2H, H<sub>e,e'</sub>), 1.62 (3H, H<sub>b,b',d</sub>), 1.28 (m, 1H, H<sub>d'</sub>), 1.10 (m, 1H, H<sub>c</sub>), 0.90 (m, 1H, H<sub>c'</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 2927 (m), 2225 (m), 1543(b), 1441(m), 1372 (s), 1262 (b), 833(s). Mass Spectrum (+ESI): *m/z* 553 [Cp<sub>2</sub>Mo{S<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>10</sub>CN)(quin)}]<sup>+</sup>.

### Synthesis of [Cp<sub>2</sub>W{S<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>10</sub>CN)(Ph)}]



ACCN (220 mg, 0.90 mmol) and phenylacetylene (0.1 cm<sup>3</sup>, 0.90 mmol) were dissolved in dry toluene (20 cm<sup>3</sup>) and heated at 90 °C under argon for 20 mins. [Cp<sub>2</sub>W(S<sub>4</sub>)] (100 mg, 0.20 mmol) in anhydrous DMF (2 cm<sup>3</sup>) was added dropwise into the reaction mixture that was heated to reflux at 100 °C for 20 h. After this time, the solvent was removed under a reduced pressure to give a reddish black solid. Column chromatography (silica gel 60, 220-440 mesh) of the solid gave, on elution with CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (95:5), the product as a single dark orange band which was collected and evaporated to dryness to give a dark orange solid. The solid was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane until the product precipitated as a dark orange solid. The solvent was removed by decantation and the product dried under reduced pressure. Yield 16 mg, 12 %. (Found: C, 51.11; H, 4.36; N, 2.56 %. Calculated for C<sub>25</sub>H<sub>25</sub>WS<sub>2</sub>N: C, 51.11; H, 4.29, N, 2.38 %). <sup>1</sup>H NMR {300 MHz, CDCl<sub>3</sub>}: δ /ppm 7.29 - 7.52 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 5.26 (s, 10H, 2×Cp), 2.16 (m, 2H, H<sub>a,a'</sub>), 1.90 (m, 2H, H<sub>e,e'</sub>), 0.88-1.69 (m, 6H, H<sub>b,b',c,c',d,d'</sub>). IR Spectrum (cm<sup>-1</sup>): (KBr disc) 2924 (s), 2230 (m), 1531 (m), 1385 (s), 1259 (m), 837 (m). Mass Spectrum (+ESI): *m/z* 587 [Cp<sub>2</sub>W{S<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>10</sub>CN)(Ph)}]<sup>+</sup>.

- 1 F. Feher, "Handbook of Preparative and Inorganic Chemistry", G. Brauer, Ed., Academic Press, New York, 1963, p. 361.
- 2 A. Dinsmore, J. H. Birks, C. D. Garner, and J. A. Joule, *J. Chem Soc., Perkin Tran.* 1, 1997, 801 - 807.