Supplementary Information

A radical pathway to synthesise Mo and W dithiolene complexes

Ai Ling Tan, Alexander J. Blake, E. Stephen Davies, Claire Wilson and C. David Garner

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. [Cp₂M(S₄)] (M = Mo or W) was synthesised from [Cp₂MCl₂] (Sigma Aldrich Company Ltd.). 1 2-Ethynylquinoxaline was synthesised by the method of Dinsmore. 2 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.

Synthesis of [Cp₂Mo{S₂C₂(CMe₂CN)(Ph)}]

AIBN (138 mg, 0.84 mmol) was dissolved in anhydrous toluene (10 cm³), phenylacetylene (0.1 cm³, 0.8 mmol) was added and the mixture stirred under an Ar atmosphere at 70 °C. A solution of [Cp₂Mo(S₄)] (100 mg, 0.28 mmol) in anhydrous DMF (2 cm³) and anhydrous toluene (5 cm³) 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 CH₂Cl₂ gave, on elution with CH₂Cl₂:CH₃OH (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 C₂₂H₂₁NMoS₂: C, 57.51; H, 4.61, N, 3.05 %). ¹H NMR {300 MHz, CDCl₃}: δ /ppm 7.15 - 7.31 (m, 5H, C₆H₅), 5.33 (s, 10H, 2×Cp), 1.50 (s, 6H, 2×CH₃). IR Spectrum (cm⁻¹): (KBr disc) 3108 (m), 2228 (m), 1600 (m), 1440 (m), 1223 (m), 1071 (s), 831 (s). Mass Spectrum (+ESI): m/z 460 [Cp₂Mo{S₂C₂(CMe₂CN)(Ph)}]⁺.
Synthesis of \([\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2\text{(CMe}_2\text{CN)(2-py)}\}]\]

This preparation was accomplished in a manner similar to that described for \([\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2\text{(CMe}_2\text{CN)(Ph)}\}]\) except that 2-ethynylpyridine (0.1 cm\(^3\), 0.8 mmol) was used in place of phenylacetylene. Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH\(_2\)Cl\(_2\) gave, on elution with CH\(_2\)Cl\(_2\):CH\(_3\)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\(_{21}\)H\(_{20}\)N\(_2\)MoS\(_2\): C, 54.78; H, 4.38, N, 6.08 %). \(^1\)H NMR \(\{300 \text{ MHz, CDCl}_3\}\): \(\delta/\text{ppm} \) 8.56 (d, \([J_{\text{H-H}} = 3.7 \text{ Hz}]\), H\(_6\)), 7.62 (t, \([J_{\text{H-H}} = 7.0 \text{ Hz}]\), H\(_4\)), 7.34 (d, \([J_{\text{H-H}} = 7.7 \text{ Hz}]\), H\(_3\)), 7.13 (t, \([J_{\text{H-H}} = 7.1 \text{ Hz}]\), H\(_5\)), 5.30 (s, 10H, 2\(\times\)Cp), 1.61 (s, 6H, 2\(\times\)CH\(_3\)). IR Spectrum (cm\(^{-1}\)): (KBr disc) 3114 (m), 2223 (m), 1582 (m), 1465 (m), 1260 (m), 1096 (s), 809 (s). Mass Spectrum (+ESI): \(m/\text{z} \) 463 \([\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2\text{(Me}_2\text{CN)(2-py)}\}]\)\(^+\).

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

This preparation was accomplished in a manner similar to that described for \([\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2\text{(CMe}_2\text{CN)(Ph)}\}]\) except that 2-ethynylquinoxaline\(^{34}\) (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\(_2\)Cl\(_2\) gave, on elution with CH\(_2\)Cl\(_2\):CH\(_3\)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 32 mg, 25% (Found: C, 56.24; H, 4.24; N, 7.77 %). Calc. for C\(_{24}\)H\(_{21}\)N\(_3\)MoS\(_2\): C, 56.35; H, 4.14, N, 8.21 %). \(^1\)H NMR \(\{300 \text{ MHz, CDCl}_3\}\): \(\delta/\text{ppm} \) 8.86 (s, H\(_3\)), 8.04 (m, H\(_5/8\)), 7.68 (d, H\(_{6/7}\)), 5.32 (s, 10H, 2\(\times\)Cp), 1.69 and 1.60 (s, 2\(\times\)3H, 2\(\times\)CH\(_3\)). IR Spectrum (cm\(^{-1}\)): (KBr disc) 3114 (m), 2223 (m), 1588 (m), 1434 (m), 1265 (m), 1116 (s), 809 (s) Mass Spectrum (+ESI): \(m/\text{z} \) 511 \([\text{Cp}_2\text{Mo}\{\text{S}_2\text{C}_2\text{(CMe}_2\text{CN)(quin)}\}]\)\(^+\).
Synthesis of [Cp₂W{S₂C₂(C₂Me₂CN)(Ph)}]

AIBN (100 mg, 0.66 mmol) was dissolved in anhydrous toluene (10 cm³), phenylacetylene (0.1 cm³, 0.8 mmol) was added and the mixture was stirred under an Ar atmosphere at 70 °C. A solution of [Cp₂W(S₄)] (60 mg, 0.14 mmol) in anhydrous DMF (2 cm³) and anhydrous toluene (5 cm³) 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 CH₂Cl₂ gave, on elution with CH₂Cl₂:CH₃OH (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 C₂₂H₂₁N₇S₂: C, 48.27; H, 3.87, N, 2.56 %). ¹H NMR {300 MHz, CDCl₃}: δ/ppm 7.09-7.33 (m, 5H, C₆H₅), 5.33 (s, 10H, 2×Cp), 1.57 (s, 6H, 2×CH₃). IR Spectrum (cm⁻¹): (KBr disc) 3103 (m), 2229 (m), 1613 (m), 1436 (m), 1255 (m), 1092 (s), 829 (s). Mass Spectrum (+ESI): m/z 548 [Cp₂W{S₂C₂(C₂Me₂CN)(Ph)}]+.

Synthesis of [Cp₂W{S₂C₂(C₂Me₂CN)(2-py)}]

This preparation was accomplished in a manner similar to that for [Cp₂W{S₂C₂(C₂Me₂CN)(Ph)}] except that 2-ethynylpyridine (0.1 cm³, 0.8 mmol). Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH₂Cl₂ gave, on elution with CH₂Cl₂:CH₃OH (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 C₂₁H₂₀N₂WS₂: C, 46.00; H, 3.68; N, 5.11 %). ¹H NMR {300 MHz, CDCl₃}: δ/ppm 8.56 (d, H₆), 7.62 (t, H₄), 7.32 (d, H₃), 7.13 (t, H₅), 5.29 (s, 10H, 2×Cp), 1.60 (s, 6H, 2×CH₃). IR Spectrum (cm⁻¹): (KBr disc) 3110 (m), 2220 (m), 1570 (m), 1460 (m), 1255 (m), 1092 (s), 809 (s). Mass Spectrum (+ESI): m/z 549 [Cp₂W{S₂C₂(C₂Me₂CN)(2-py)}]⁺.
Synthesis of [Cp₂W{S₂C₂(CMe₂CN)(quin)}]

![Chemical structure of Cp₂W{S₂C₂(CMe₂CN)(quin)}](attachment:chemistry.png)

This preparation was similar to that of [Cp₂W{S₂C₂(CMe₂CN)(Ph)}] except that 2-ethynylquinoxaline₃⁴ (22 mg, 0.14 mmol) was used in place of phenylacetylene. Column chromatography (silica gel 60, 220-440 mesh) of the crude product in CH₂Cl₂ gave, on elution with CH₂Cl₂ and CH₃OH (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 C₂₄H₂₁N₃WS₂: C, 48.09; H, 3.53; N, 7.01%). ¹H NMR {300 MHz, CDCl₃}: δ /ppm 8.85 (s, H₃), 8.03 (m, H₅/₈), 7.68 (d, H₆/₇), 5.29 (s, 10H, 2×Cp), 1.69 (s, 6H, 2×CH₃). IR Spectrum (cm⁻¹): (KBr disc) 3099 (m), 2225 (m), 1500 (m), 1382 (m), 1264 (m), 1116 (s), 838 (s). Mass Spectrum (+ESI): m/z 599 [Cp₂W{S₂C₂(CMe₂CN)(quin)}]+.

Synthesis of [Cp₂Mo{S₂C₂(C₆H₁₀CN)(Ph)}]

ACCN (220 mg, 0.90 mmol) and phenylacetylene (0.1 cm³, 0.90 mmol) were dissolved in dry toluene (20 cm³) and heated at 90 °C under argon for 20 mins. [Cp₂Mo(S₄)] (80 mg, 0.23 mmol) in anhydrous DMF (2 cm³) 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 [Cp₂Mo{S₂C₂(C₆H₁₀CN)(Ph)}] in CH₂Cl₂. 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 C₂₅H₂₅MoS₂N: C, 60.11; H, 5.04, N, 2.80 %). ¹H NMR {300 MHz, CDCl₃}: δ /ppm 7.21 - 7.42 (m, 5H, C₆H₅), 5.32 (s, 10H, 2×Cp), 2.03 (m, 2H, Ha,a'), 1.82 (m, 2H, He,e'), 1.62 (m, 3H, Hb,b',d), 1.30 (m, 1H, Hc'), 1.09 (m, 1H, Hc), 0.88 (m, 1H, Hc'). IR Spectrum (cm⁻¹): (KBr disc) 2923 (m), 2228 (m), 1634 (m), 1381 (s), 1261 (m), 811(s). Mass Spectrum (+ESI): m/z 501 [Cp₂Mo{S₂C₂(C₆H₁₀CN)(Ph)}]+.
Synthesis of [Cp₂Mo{S₂C₂(C₆H₁₀CN)(2-py)}]

ACCN (270 mg, 1.10 mmol) and 2-ethynylpyridine (0.1 cm³, 0.90 mmol) were dissolved in dry toluene (20 cm³) and heated at 90 °C under argon for 20 mins. [Cp₂Mo(S₄)] (100 mg, 0.34 mmol) in anhydrous DMF (2 cm³) 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 CH₂Cl₂ 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 C₂₄H₂₄MoS₂N₂: C, 57.85; H, 4.83, N, 5.60 %). \(^{1}H\) NMR \((300 MHz, CDCl₃)\): δ /ppm 8.57 (d, \([J_H-H] = 4.1 Hz\), H₆), 7.63 (td, \([J_{1(H-H)}] = 7.8 Hz, J_{2(H-H)} = 1.8 Hz\) ), H⁵), 7.35 (d, \([J_H-H] = 7.5 Hz\), H³), 7.14 (t, \([J_H-H] = 5.9 Hz\), H²), 5.30 (s, 10H, 2×Cp), 2.12 (m, 2H, Hₐ,a), 1.96 (td, \(J_{1(H-H)} = 11.9, J_{2(H-H)} = 5.9 Hz\), 2H, Hₐ,a), 1.62 (m, 3H, Hₐ,a), 1.28 (m, 1H, Hₐ,a). IR Spectrum (cm⁻¹): (KBr disc) 2927 (m), 2217 (m), 1646 (b), 1460 (m), 1382 (s), 1259 (b), 809 (s). Mass Spectrum (+ESI): \(m/z\) 500 [Cp₂Mo{S₂C₂(C₆H₁₀CN)(2-py)}].

Synthesis of [Cp₂Mo{S₂C₂(C₆H₁₀CN)(quin)}]

ACCN (270 mg, 1.10 mmol) and 2-ethynylquinoxaline (100 mg, 0.7 mmol) were dissolved in dry toluene (20 cm³) and heated at 90 °C under argon for 20 mins. [Cp₂Mo(S₄)] (100 mg, 0.34 mmol) in anhydrous DMF (2 cm³) 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 CH₂Cl₂ 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 C₂₇H₂₄MoS₂N₃: C, 58.79; H, 4.57, N, 7.60 %). ¹H NMR {300 MHz, CDCl₃}: δ/ppm 8.87 (s, H₃), 8.06 (m, H₅/₈), 7.69 (m, H₆/₇), 5.34 (s, 10H, 2×Cp), 2.26 (m, 2H, Hₐ,a' ), 2.06 (td, [J₁ (H-H) = 11.4, J₂ (H-H) = 5.4 Hz], 2H, Hₜ,e'), 1.62 (3H, Hₕ,b,b'), 1.28 (m, 1H, Hₙ,a'), 1.10 (m, 1H, Hₙ), 0.90 (m, 1H, Hₙ). IR Spectrum (cm⁻¹): (KBr disc) 2927 (m), 2225 (m), 1543(b), 1441(m), 1372 (s), 1262 (b), 833(s). Mass Spectrum (+ESI): m/z 553 [Cp₂Mo{S₂C₂(C₆H₁₀CN)(quin)}]+.

Synthesis of [Cp₂W{S₂C₂(C₆H₁₀CN)(Ph)}]

ACCN (220 mg, 0.90 mmol) and phenylacetylene (0.1 cm³, 0.90 mmol) were dissolved in dry toluene (20 cm³) and heated at 90 °C under argon for 20 mins. [Cp₂W(S₄)] (100 mg, 0.20 mmol) in anhydrous DMF (2 cm³) 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 CH₂Cl₂ 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 CH₂Cl₂ 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, 2.38 %). Calculated for C₂₅H₂₅WS₂N: C, 51.11; H, 4.29, N, 2.38 %. ¹H NMR {300 MHz, CDCl₃}: δ/ppm 7.29 - 7.52 (m, 5H, C₆H₅), 5.26 (s, 10H, 2×Cp), 2.16 (m, 2H, Hₐ,a' ), 1.90 (m, 2H, Hₕ,e'), 0.88-1.69 (m, 6H, Hₕ,b,b',c,c',d,d'). IR Spectrum (cm⁻¹): (KBr disc) 2924 (s), 2230 (m), 1531 (m), 1385 (s), 1259 (m), 837 (m). Mass Spectrum (+ESI): m/z 587 [Cp₂W{S₂C₂(C₆H₁₀CN)(Ph)}]+.