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New cyclopentadienyl molybdenum polynuclear clusters from ring opening of Woollins' reagent via phosphorus–selenium bond scission, phosphorus–phosphorus coupling and deselenation pathways

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ABSTRACT

Cothermolysis of $[(Ph)P(Se)(\mu\text{-}Se)]_2$ or Woollins' reagent (WR) with $Cp_2Mo_2(CO)_4$ (**2**) in toluene at 110 °C led to the isolation of three different metal clusters, $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3]$ (**3**), $Cp_4Mo_4(CO)_3(\mu\text{-}Se)_4$ (**4**) and a pair of isomer complexes of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**5a** and 5**b**) in 17.5%, 3.1% and 4.9% yields, respectively. A similar reaction at 70 °C gave only **5a** and 5**b** in 2.0% and 4.9% yields, respectively. All complexes have been fully characterized *via* NMR, IR and ESI mass spectroscopy. Molecular structures of **3**, **4** and **5a** were confirmed by single crystal X-ray diffraction analyses. A variable temperature ^1H NMR study of **4** was carried out. Finally, a free-radical addition pathway by selenation of WR was postulated.

1. Introduction

Reaction of mixed pnicogen/chalcogen ligands towards organometallic complexes have been investigated intensively for the past two decades [1–22]. These mixed donor heterocyclic ligands were capable of generating new coordination modes with metal complexes resulting in the formation of novel polynuclear clusters.

To date, most of the reported mixed pnicogen/chalcogen transition-metal complexes were generated from mixed P/S ligands such as P_4S_3 [23], $R_2P(S)P(S)R_2$ (R = Me, Et) [24] and $[(MeOPh)P(S)(\mu\text{-}S)]_2$ (Lawesson's reagent) [25a,b]. So far a limited amount of work has been accounted for the analogous mixed P/Se ligands. As a comparative study, Woollins' reagent, $[(Ph)P(Se)(\mu\text{-}Se)]_2$, the selenium analogue of Lawesson's reagent, which acts as a source for P/Se ligand has prompted us to investigated its reactivity towards $Cp_2Cr_2(CO)_4$ [21]. Herein, as an extension to our investigation, we would like to report the reactivity of Woollins' reagent towards the Mo cogener, $Cp_2Mo_2(CO)_4$ (**2**).

2. Experimental

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of argon in a Vacuum Atmosphere Dribox. ^1H, ^{13}C and ^{31}P NMR spectra were measured on JEOL Lambda and ECA 400 MHz spectrometers. ^1H and ^{13}C chemical shifts were referenced to residual C_6H_6 in C_6D_6 and ^{31}P chemical shifts to 85% aqueous H_3PO_4 (external standard) for $^{31}P\{^1H\}$. IR spectra in Nujol mulls were measured in the range of 4000–400 cm^{-1} by means of a Perkin–Elmer 2000 FTIR instrument. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University except for CH which was done by in-house microanalytical laboratory using a Perkin–Elmer 2400 Series II CHNS System. Mass spectrometric measurements, performed by direct injection using electrospray ionization (ESI), were made on an Agilent 6230 LCMS instrument. Electrospray (high resolution) mass spectrometric measurements were obtained on an Accurate Mass Q-Tof spectrometer. All solvents were dried distilled of sodium/benzophenone under nitrogen prior to use. Silica gel (Merck Kieselgel 60, 35–70 mesh) and Celite (Fluka AG) were activated at 140 °C overnight before chromatographic use. 1,3,2,4-dithiadiphosphetane 2,4-diselenides (Woollins' reagent) was purchased from Sigma–

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Aldrich. $[CpMo(CO)_3]_2$ was synthesized as described by Manning [26] from molybdenum hexacarbonyl (99% purity from Sigma).

2.1. Reaction of $Cp_2Mo_2(CO)_4$ with Woollins' reagent at 110 °C

A reddish brown solution of $Cp_2Mo_2(CO)_4$ (**2**) (300 mg, 0.612 mmol) and Woollins' reagent (326 mg, 0.612 mmol) in toluene (~25 mL) was refluxed with stirring for 4 h. The resultant dark purplish brown reaction mixture was filtered through a sintered-glass funnel to remove an uncharacterized non-Cp containing brown residue (279 mg). The filtrate was concentrated to *ca.* 3–4 mL and loaded onto a silica gel column (1.5 cm x 12 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) An orange pink fraction was eluted with *n*-hexane–toluene (2:1.5, 35 mL) which when concentrated to dryness gave unreacted fine orange red solids of $Cp_2Mo_2(CO)_4$ (**2**) (28 mg, 0.064 mmol, 10.5% recovery).

(ii) An orange brown fraction was eluted with *n*-hexane–toluene (1:1.5, 40 mL) which when concentrated to dryness gave dark reddish brown crystalline solids of $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}]$ (**3**) (114 mg, 0.107 mmol, 17.5% yield). Anal. Found: ^{1}H NMR (benzene-d_6): δ 4.39, 4.72, 5.34, 5.60 (s, Cp), δ 6.78–7.95 (m, C_6H_5). ^{13}C NMR (benzene-d_6): δ 88.47, 89.43, 89.54, 90.37 (Cp), δ 126.04, 128.90, 129.67, 130.57, 132.43 (C_6H_5). ^{31}P NMR (benzene-d_6): δ 158.91, 159.52, 160.79, 167.59. HR-MS ESI$^+$ (*m*/*z*): (^{96}Mo, ^{80}Se): 1070.6110 $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_3\}]$, 991 $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh)\}\{(\mu\text{-}Se)(PPh)_3\}]$, 964 $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)_2\}]$, 914 $[Cp_2Mo_2\{(\mu\text{-}Se)_2(P)\}\{(\mu\text{-}Se)(PPh)_3\}]$, 883 $[Cp_2Mo_2(\mu\text{-}Se)_2\{(\mu\text{-}Se)(PPh)_3\}]$, 854 $[Cp_2Mo_2\{(\mu\text{-}Se)_2(PPh(Se))\}\{(\mu\text{-}Se)(PPh)\}]$, 670 $[Cp_2Mo_2(\mu\text{-}Se)_2(PPh(Se))]$, 589 $[Cp_2Mo_2(\mu\text{-}Se)_2(PPh)]$, 559 $[Cp_2Mo_2(\mu\text{-}Se)_3]$. *Anal.* Calc. for $C_{34}H_{30}Mo_2P_4Se_4$: C, 38.01; H, 2.81; Mo, 18.24; P, 11.54; Se, 29.79. Found: C, 37.92; H, 2.75; Mo, 18.20; P, 11.83; Se, 29.56%.

(iii) An orange brown fraction was eluted with *n*-hexane–toluene (1:1.5, 52 mL) which when concentrated to dryness gave an uncharacterized brown amorphous solid (42 mg). Anal. Found: ^{1}H NMR (benzene-d_6): δ 5.26, 5.37 (s, Cp), δ 7.01–7.13 (m, C_6H_5). ^{13}C NMR (benzene-d_6): δ 94.77, 94.89 (Cp), δ 126.03, 128.90, 129.67 (C_6H_5). I.R.: *v* at 1276w, 1261vw, 1177vw, 1157vw, 1106w, 1092w, 1056w, 1024w, 1005w, 940vw, 918vw, 876vw, 841vw, 806w, 740w, 728w, 700w, 688w, 639vw cm^{-1} (Nujol).

(iv) A blue fraction was eluted with *n*-hexane–toluene (1:1.75, 12 mL) which when concentrated to dryness gave dark greenish blue oily solids of $Cp_4Mo_4(CO)_3Se_4$ (**4**) (19 mg, 0.019 mmol, 3.1% yield). Anal. Found: ^{1}H NMR (benzene-d_6): δ 4.48, 4.49, 4.53, 4.55, 4.56, 4.567, 4.57, 4.71, 5.43, 5.49, 5.52, 5.63 (m, Cp); ^{13}C NMR (benzene-d_6): δ 89.76, 89.86, 90.73, 90.77, 91.01, 91.09, 91.64, 91.73, 92.01, 92.07, 92.43, 92.59 (Cp), δ 196.02, 230.02 (CO). I.R.: *v* (CO) at 1933vs, 1870s cm^{-1} and other peaks at 805 m, 739w, 723w, 552vw, 534w, 510vw cm^{-1} (Nujol). HR-MS ESI$^+$ (*m*/*z*): (^{96}Mo, ^{80}Se): 1044.0000 $Cp_4Mo_4(CO)_3Se_4$, 1018 $Cp_4Mo_4(CO)_2Se_4$, 989 $Cp_4Mo_4(CO)Se_4$, 961 $Cp_4Mo_4Se_4$, 895 $Cp_3Mo_4Se_4$, 799 $Cp_3Mo_3Se_4$, 735 $Cp_2Mo_3Se_4$, 669 $CpMo_3Se_4$/$Cp_3Mo_3(CO)Se_2$, 641 $Cp_3Mo_3Se_2$, 636 $Cp_2Mo_2Se_4$, 604 Mo_3Se_4, 590 $Cp_2Mo_2(CO)_4Se_2$, 576 $Cp_2Mo_3Se_2$, 525 Mo_3Se_3, 445 Mo_3Se_2, 374 $CpMo(CO)_2Se_2$, 369 Mo_3Se, 289 Mo_3. *Anal.* Calc. for $C_{23}H_{20}Mo_4O_3Se_4$: C, 26.15; H, 1.91; Mo, 37.11; Se, 30.29. Found: C, 25.98; H, 1.93; Mo, 37.05; Se, 30.35%.

(v) A pink fraction was eluted with *n*-hexane–toluene (1:2, 54 mL) which when concentrated to dryness gave pink crystalline solids of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**5a**) (14 mg, 0.013 mmol, 2.1% yield). Anal. Found: ^{1}H NMR (benzene-d_6): δ 4.57, 4.78, 4.82 (s, Cp), δ 7.01–7.13, 8.91–8.95 (m, C_6H_5). ^{13}C NMR (benzene-d_6): δ 90.55, 91.15, 94.04 (Cp), δ 126.03, 128.90, 129.67, 138.23 (C_6H_5). ^{31}P NMR (benzene-d_6): δ 118.55, 120.49. I.R.: ν(CO) at 1974s, 1921vs, 1845s cm^{-1}; other peaks at 1157m, 1096m, 1022m, 821w, 795w, 749vw, 739vw, 724w, 697vw, 554vw, 511vw, 489w, 474w, 466w, 448w, 423w, 408vw cm^{-1} (Nujol). HR-MS ESI$^+$ (*m*/*z*): (^{96}Mo, ^{80}Se): 1109.8780 $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$, 941 $Cp_3Mo_3(CO)_2[Se_3(PPh)]$, 837 $Cp_3Mo_3(CO)_2Se_3$, 733 $Cp_3Mo_3(CO)Se_2$, 662 $Cp_2Mo_3(CO)Se_2$, 583 $Cp_2Mo_3(CO)Se$. *Anal.* Calc. for $C_{31}H_{25}Mo_3O_4P_2Se_3$: C, 33.26; H, 2.25; Mo, 26.26; P, 11.07; Se, 21.44. Found: C, 33.52; H, 2.29; Mo, 26.25; P, 11.10; Se, 21.58%.

(vi) A purplish pink fraction was eluted with toluene (25 mL) which when concentrated to dryness gave dark purplish pink crystalline solids of the isomer product of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**5b**)(19 mg, 0.017 mmol, 2.8% yield). Anal. Found: ^{1}H NMR (benzene-d_6): δ 4.58, 4.77, 4.85 (s, Cp), δ 7.01–7.14 (m, C_6H_5). ^{13}C NMR (benzene-d_6): δ 90.16, 90.72, 94.27 (Cp), δ 126.03, 128.90, 129.67, 133.45 (C_6H_5). ^{31}P NMR (benzene-d_6): δ 118.73, 120.71. I.R.: ν(CO) at 1961m, 1926s, 1847m, 1156m, 1106m, 1050m, 1021m, 876w, 818w, 743vw, 728vw, 693vw, 669vw, 551vw, 525vw, 518vw, 473vw, 466vw, 458vw, 442vw cm^{-1} (Nujol). *Anal.* Calc. for $C_{31}H_{25}Mo_3O_4P_2Se_3$: C, 33.26; H, 2.25; Mo, 26.26; P, 11.07; Se, 21.44. Found: C, 33.37; H, 2.31; Mo, 26.28; P, 11.13; Se, 21.50%. A dark brown ring remained unmoved on the top of the column.

2.2. Reaction of $Cp_2Mo_2(CO)_4$ with Woollins' reagent at 70 °C

$Cp_2Mo_2(CO)_4$ was generated *in situ* by refluxing the $Cp_2Mo_2(CO)_6$ (200 mg, 0.408 mmol) in toluene (~20 mL) at 120 °C for 20 h under stirring. After the solution has cooled down to room temperature, Woollins' reagent (230 mg, 0.408 mmol) was added to it. The reaction mixture was stirred at 70 °C for 2 h. The resultant brownish purple mixture was filtered through a sintered-glass funnel. The filtrate was concentrated to dryness and then redissolved in THF (~2 mL) followed by absorbed onto silica gel (~0.5 g). The dark brownish purple slurry was evacuated to dryness under *vacuo* and chromatographed onto a silica gel column (1.5 cm × 10 cm) prepared in *n*-hexane. The following fractions were eluted:

(i) A pinkish red fraction was eluted with *n*-hexane–toluene (2.5:1, 32 mL) which when concentrated to dryness gave the carbonylated $Cp_2Mo_2(CO)_6$ (**1**) (23 mg, 0.0469 mmol, 11.5% recovery) was obtained.

(ii) A brownish orange fraction was eluted with *n*-hexane–toluene (2:1, 20 mL) which when concentrated to dryness, the unreacted $Cp_2Mo_2(CO)_4$ (**2**) (10 mg, 0.023 mmol, 5.6% recovery) was obtained.

(iii) A brownish orange fraction was eluted with *n*-hexane–toluene (1:1.5, 32 mL) which when concentrated to dryness, gave an uncharacterized Cp containing red precipitate (39 mg). Anal. Found: ^{1}H NMR (benzene-d_6): δ 4.27(s, Cp), δ 6.97–7.06, 7.11–7.13 (m, C_6H_5). ^{13}CNMR (benzene-d_6): δ 90.77, 91.42, 91.94, 92.46 (Cp), δ 128.15, 128.63, 138.22, (C_6H_5). ^{31}P NMR (benzene-d_6): δ 63.35, 63.86, 174.47, 176.34, 236.90, 237.41.

(iv) An orange pink fraction was eluted with toluene (13 mL) which when concentrated to dryness gave $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**5a**) (9 mg, 0.008 mmol, 2.0% yield).

(v) A purple fraction was eluted with ether (13 mL) which when concentrated to dryness gave the isomer product of $Cp_3Mo_3(CO)_4[Se_3(PPh)_2]$ (**5b**) (22 mg, 0.02 mmol, 4.9% yield). A dark brown rim remained unmoved on the top of the column.