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Stabilisation of an Unusual P_2Se_2 Aggregate by Cyclopentadienyl Chromium Carbonyl Fragments. Synthesis and Crystal Structure of $Cp_4Cr_4(CO)_8(P_2Se_2)$

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The reaction of $[CpCr(CO)_3]_2$ with P_4Se_3 at ambient temperature produced $Cp_4Cr_4(CO)_8(P_2Se_2)$, a tetrachromium complex possessing an unusual "open-book" structure.

There is current intense interest in the role of main group heteroatoms and polyatomic aggregates in transition metal complexes and clusters.[1] Our work in this area has involved the reaction of $[CpCr(CO)_3]_2$ **1** with the chalcogens S_8 [2] and Se_8, [3] the pnicogens P_4 [4–5] and As_4 [6] and lately with tetraphosphorus trisulphide P_4S_3.[7] This paper describes the results of the reaction of **1** with P_4Se_3.

$[CpCr(CO)_3]_2$ and P_4Se_3 (1 mol equiv.) in toluene were allowed to react at ambient temperature for 12 days. The product mixture was concentrated to dryness and extracted with THF, leaving behind some P_4Se_3 (27% recovery). Column chromatography of the extracts on silica gel led to the elution of (i) $CpCr(CO)_2P_3$ as a yellow solution in 2:1 *n*-hexane–toluene, which gave yellow crystals (13.6%), characterised as previously described;† (ii) P_4Se_3 as an orange solution in 1:1 *n*-hexane–toluene, which gave brownish orange crystalline solids of P_4Se_3 (5.6% recovery); (iii) $Cp_4Cr_4(CO)_8(P_2Se_2)$ **2** as a reddish brown solution with 2:3 *n*-hexane–toluene, from which were isolated dark brown crystals (33.5%), characterised by analytical and spectroscopic methods;‡ and (iv) $Cp_4Cr_4(CO)_9(P_4Se_3)$ as a yellowish brown solution in 1:3 *n*-hexane–toluene, from which were isolated dark brown crystals (43.8%), characterised by analytical spectroscopic and single crystal X-ray diffraction analyses (not presented here because of its close resemblance to the S analogue[7]). Dark brown thick triangular plates of **2** suitable for a single-crystal X-ray structural analysis§ were obtained from a solution in toluene–*n*-hexane after 10 days at −28 °C.

† *NMR spectral data:*[4] ^{1}H (100 MHz, C_6D_6, residual C_6H_6): δ(Cp) 3.92. ^{13}C (25 MHz, C_6D_6, residual C_6H_6): δ(Cp) 84.91, δ(CO) 233.74. TLC on Merck Kieselgel $^{60}F_{254}$ plates *versus* an authentic sample: R_f 0.65 with 3:2 *n*-hexane–toluene as eluent.

‡ Satisfactory elemental analysis. ^{1}H NMR (270 MHz, C_6D_6, 25 °C, residual C_6H_6): δ(Cp) 4.52 and 4.45. ^{13}C NMR (26.04 MHz, C_6D_6, residual C_6H_6): δ(Cp) 93.10 and 89.91. ^{31}P NMR (96.15 MHz, C_6D_6, H_3PO_4): δ 333.24. IR (toluene): ν_{CO}/cm^{-1} 1943vs, 1889s.

§ *Crystal data:* Molecular formula = $Cp_4Cr_4(CO)_8(P_2Se_2)$. M_r = 912.3, orthorhombic, space group $C222_1$, a = 14.901(6), b = 14.889(5), c = 13.686(4) A, V = 3036(2) A , Z = 4, ρ(calc.) = 1.996 Mg m^{-3}, $F(000)$ = 1784, λ(MoK$_\alpha$) = 0.71073 A, T = 22 °C, crystal dimensions: 0.16 × 0.14 × 0.26 mm, μ = 3.946 mm^{-1}. Siemens P4 diffractometer, ω scan type. Of 2410 reflections measured, 1721 [$F > 4\sigma(F)$] were used in refinement. The crystal used for unit cell determination and data collection was coated with epoxy glue to prevent decomposition in air. Thirty six strong reflections were used for accurate determination of the unit cell parameters. Raw intensities were processed for Lorentz-polarization effects and decay. Absorption correction did not improve the quality of the data and is omitted. The structure was solved by direct methods of the Siemens SHELXTL/PC programs. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on the parent C atoms with fixed U of 0.08 A^2. Computations were performed using an IBM 486PC. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated.[8] Final R = 0.044 (R_w = 0.051) for the correct enantiomer (Flack x parameter = 0.00 in SHELXL93 programs). Full lists of bond lengths, bond angles and atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC), see Notice to Authors, *Mendeleev Commun.*, 1995, issue 1.

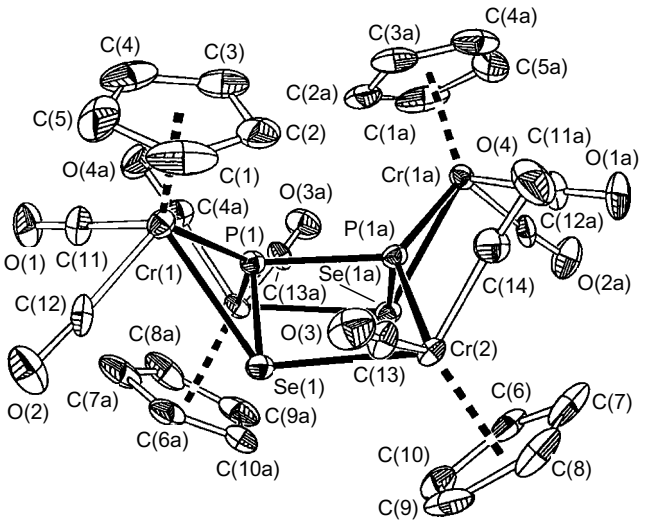

Fig. 1 Molecular structure of $[CpCr(CO)_2]_4P_2Se_2$ (**2**). Some bond lengths/Å: P(1)–P(1a) 2.237(5), Se(1)–Cr(1) 2.566(2), Se(1)–Cr(2) 2.575(2), Se(1)–P(1) 2.250(3), Cr(1)–P(1) 2.340(3), Cr(2)–P(1a) 2.393(3), Cr(2a)–P(1) 2.393(3). Bond angles/° at P(1): Se(1)–P(1)–Cr(1), 68.0(1), Se(1)–P(1)–Cr(2a) 119.4(1), Cr(1)–P(1)–Cr(2a) 138.8(1), Se(1)–P(1)–P(1a) 83.5(1), Cr(1)–P(1)–P(1a) 117.2(2), Cr(2a)–P(1)–P(1a) 104.0(2); at Se(1): Cr(1)–Se(1)–Cr(2) 117.1(1), Cr(1)–Se(1)–P(1) 57.7(1), Cr(2)–Se(1)–P(1) 98.1(1); and others: Se(1)–Cr(1)–P(1) 54.4(1), Se(1)–Cr(2)–P(1a) 73.8(1).

The absolute molecular structure of **2**, illustrated in Fig. 1, possesses an unusual "open-book" framework with a P–P backbone, joining two CrP_2Se trapezoidal planes separated by a dihedral angle of 119.4°. A two-fold axis of symmetry passes through the mid-point of the P–P backbone. The PSe edges of the trapezoids are each η^2-bonded to a $CpCr(CO)_2$ fragment. Thus, each of the Cr atoms assumes a four-legged piano stool configuration. Each of the P atoms is four-coordinate while the Se atoms are each three-coordinate.

The P–P bond distance of 2.237(5) A is very close to those in the P_4Se_3 cage (mean 2.25 A).[9] Known values of P–P bond lengths average 2.22 A in the P_{10} core of $[CpCr(CO)_2]_5P_{10}$ [5] and 2.21 A in P_4 vapour.[10] The P–Se distance of 2.250(3) A is very close to that in the intact P_4Se_3 cage (mean 2.24 A). The Cr–P distances [2.340(3) and 2.393(3) A] fall within the range of 2.341–2.494 A observed for other CpCr complexes with phosphorus ligands.[4,5] The Cr–Se distances [2.566(2) A and 2.575(2) A] are longer than those observed in the (μ-η^2-Se_2) complex $Cp_2Cr_2(CO)_4Se_2$ (2.538–2.551 A)[3] or in the cubanes $Cp_4Cr_4Se_2(CO)_2$ (2.317–2.400 A) and $Cp_4Cr_4Se_2O_2$ (2.441–2.462 A).[11]

The structure of **2** indicates that in this reaction the P_4Se_3 cage molecule can be considered to have undergone two P–P and two P–Se bond cleavages (Fig. 2), resulting in the extrusion of a PSeP fragment, with subsequent or concomitant coordination of four $CpCr(CO)_2$ fragments to each of the atoms of the Se–P–P–Se aggregate. The approximately Z-shaped conformation of this four-atom unit and its manner of bonding to the CpCr fragments is an unusual feature not observed before in reactions of the P_4E_3 (E = S, Se) molecules. In our previous study of P_4S_3, the cage underwent multiple bond cleavages with extensive rearrangement cum coordination of $CpCr(CO)_n$ ($n = 2, 3$) fragments to yield the $Cp_4Cr_4(CO)_9(P_4S_3)$ complex.[7] The stabilisation of a P_2Se_2 main group element fragment by organotransition metals, as found in **2**, is as yet unprecedented. Indeed, these $CpCr(CO)_3^{\cdot}$ radical-initated reactions of P_4E_3 tend to produce tetranuclear complexes with rather novel features and geometries. The present results illustrate the potential role of cage molecules like P_4Se_3 in the building of transition metal-main group clusters, which are currently of interest in the extensive area of materials science.

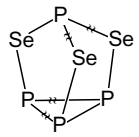

Fig. 2 Bond cleavage of P_4Se_3.

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