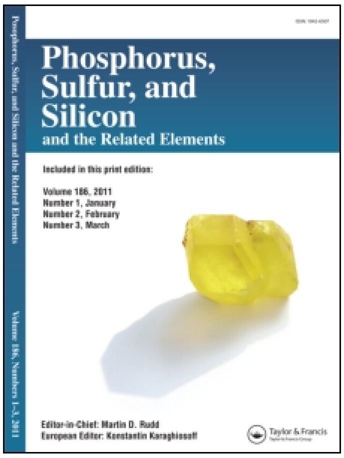

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Chromium Cluster Complexes from Cage-Opening of Polychalcogen-Pnicogen Molecules

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To cite this Article Goh, Lai Yoong , Wei, Chen and Wong, Richard C. S.(1994) 'Chromium Cluster Complexes from Cage-Opening of Polychalcogen-Pnicogen Molecules', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 209 — 212

To link to this Article: DOI: 10.1080/10426509408021818

URL: http://dx.doi.org/10.1080/10426509408021818

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 209–212
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CHROMIUM CLUSTER COMPLEXES FROM CAGE-OPENING OF POLYCHALCOGEN-PNICOGEN MOLECULES

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Abstract The reactions of $[CpCr(CO)_3]_2$ with P_4E_3 (E = S, Se) are described, with the structural features and thermal stability of the novel tetrachromium complexes $Cp_4Cr_4(CO)_9(P_4E_3)$ (E = S, Se) and $Cp_4Cr_4(CO)_8(P_2Se_2)$ being highlighted.

INTRODUCTION

Our studies on the reactivity of $[CpCr(CO)_3]_2$ towards Groups 15 and 16 main group elements[1-5], have been extended to the P_4E_3 (E = S, Se) cage molecules.

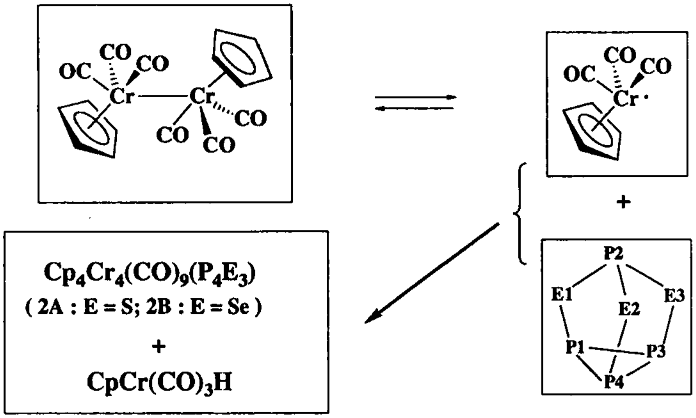
In its reactions with transition metals, the P_4E_3 molecules have been observed to undergo both nondisruptive and disruptive processes, depending on the oxidation state and ligand environment of the metal atom. Thus, the P_4E_3 molecule either coordinates intact via its apical P atom, or fragments extensively, resulting in complexes containing P_3, P_2S_3 and P_4S ligands[6]. We describe below cases where P_4E_3 undergoes multiple bond cleavage without fragmentation to produce novel tetrachromium complexes.

THE REACTIONS

With P_4S_3

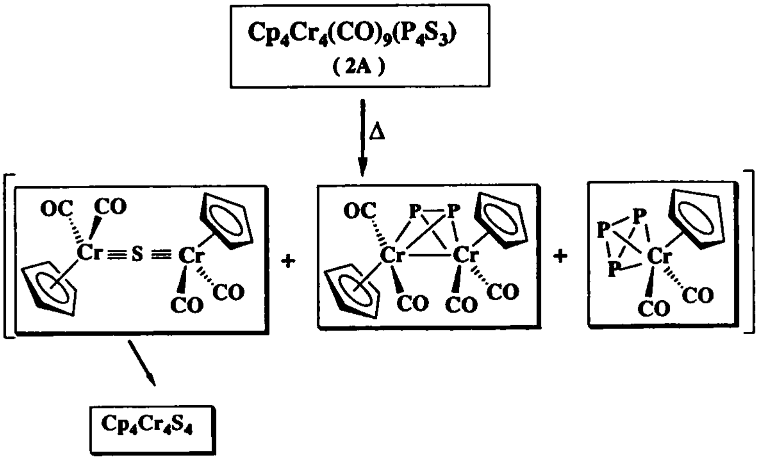
An ambient temperature reaction of $[CpCr(CO)_3]_2$ (**1**) with one mole equivalent of P_4S_3 for 13 days produces the tetrachromium complex $Cp_4Cr_4(CO)_9(P_4S_3)$ (**2A**) in *ca.* 66% yield. In view of the facile dissociation of **1** in solution into the 17-electron monomeric species $[CpCr(CO)_3.]$, it is conceivable that the reaction proceeds via a radical attack on the P_4S_3 cage, as illustrated in Scheme 1. Other products include $[CpCr(CO)_2]_2S$ (**3**) (13%), $CpCr(CO)_2P_3$ (**4**) (2%) and $CpCr(CO)_3H$ (**5**) (19%). In a similar reaction at 60 °C for 3 h, the yield of **2A** was substantially reduced to 22%, with an increased yield of **3** (36%) and the formation of the cubane complex $Cp_4Cr_4S_4$ (**6**) (7%), accompanied by lower yields of **4** (*ca.* 1%) and **5** (3%). This variation in product composition agrees with independent observations on the thermolytic degradaton of **2A** at 80 °C for 3.5 h to **3** (23%), **4** (10%), **6** (57%) and $[CpCr(CO)_2]_2P_2$ (**7**) (10%) (see Scheme 2).

Scheme 1



The isolation of the hydride **5** was indeed unexpected. It was characterised spectrally, chromatographically via TLC *vis-a-vis* an authentic sample and by single crystal X-ray diffraction analysis. One may speculate that the [$CpCr(CO)_3$.] radical trapped inside the P_4S_3 cage is able to abstract a H atom from the solvent. In this context, we have observed that **5** was not formed in the presence of isoprene.

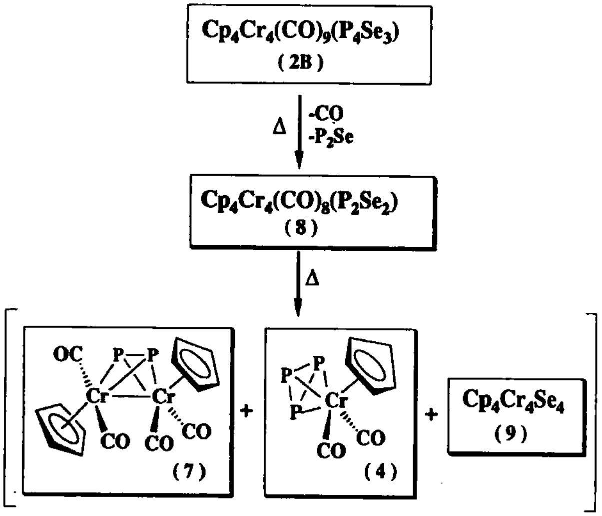
Scheme 2



With P_4Se_3

The reaction of **1** with one molar equivalent of P_4Se_3 at ambient temperature for 6 days produced a mixture of $Cp_4Cr_4(CO)_9(P_4Se_3)$ (**2B**) (48%), $Cp_4Cr_4(CO)_8(P_2Se_2)$ (**8**) (13%), **4** (8%) and **7** (16%) and a small amount of the hydride **5**. A similar reaction for 12 days yielded **2B** (31%), **8** (34%), **4** (14%) and $Cp_4Cr_4Se_4$ (**9**) (*ca.* 1 %). These observations are in agreement with the thermal degradation of **2B** which gave after 4 h at 60 °C, the complexes **8** (51%), **4** (5%), **7** (10%) and **9** (13%) (see Scheme 3).

Scheme 3



THE STRUCTURES OF 2

The complexes **2A** and **2B** possess strikingly similar molecular structures shown in Figure 1 for **2A**. It is seen that P_4S_3 has undergone cleavage of P2-S1, P4-S2 and P3-P4 bonds, with concomitant bond formation between P2 and P4, giving a five-membered P_4S ring with two external S atoms, viz. S1 at P1 and S2 at P2. Together with Cr4, this five-membered ring forms a bicyclo [2.1.1] system, possessing common vertices at P3 and P4. The P_4S ring bridges four $[CpCr(CO)_n]$ (n = 2 or 3) fragments through its four P atoms. Each of the Cr atoms is five-coordinate, possessing a four-legged piano stool geometry. Thus Cr3, coordinated to one atom of the P_4S_3 ligand, is linked to three CO groups, while the other three Cr atoms, each coordinated to two atoms of the P_4S_3 ligand, is linked to two CO groups.

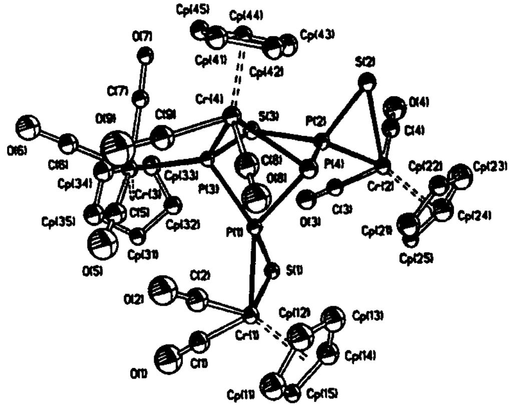


Figure 1
Molecular structure of 2A

The molecular structure of **8** will be presented if solved in time for the symposium.

Concluding Remarks

Such an example of multiple bond cleavage without fragmentation of the P_4E_3 cage by a transition metal complex as found in **2**, has not hitherto been observed. Slight cage rearrangement has occurred in the insertion of a $Cr(CO)_5$ fragment into the isostructural Zintl ion As_7^{3-}[7], and of three Ni(CO) fragments into Sb_7^{3-}[8]. The extensive cage-opening cum structural rearrangement of the P_4E_3 cage described here may be attributed to the unusual reactivity of the radical-like 17-electron $[CpCr(CO)_3]$ fragment, as was observed in the formation of the polyphosphidochromium cluster $[\{CpCr(CO)_2\}_5P_{10}]$ from elemental P_4.[5]

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