

A New Type of Polycyclophosphidochromium Cluster, $[(\text{Cp})\text{Cr}(\text{CO})_2]_5\text{P}_{10}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). First Observation of Polycyclic P-to-M Coordination

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The co-thermolysis of $[(\text{Cp})\text{Cr}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with P_4 forms $[(\text{Cp})\text{Cr}(\text{CO})_2]_5\text{P}_{10}$, a new paramagnetic structure with a P_{10} core, which represents the first example of polycyclic phosphorus-to-metal coordination.

Bare phosphorus atoms and aggregates as ligands in transition-metal complexes are of current interest.¹⁻³ The most common source of these ligands is the element P_4 itself, and the complexes are frequently encountered with P in bonding modes, μ_3 - and μ_4 -P; μ - η^2 - P_2 , η^3 - P_3 , η^1 - P_4 and η^2 - P_4 .¹ Less common types include the distorted cubanes of $\text{Co}_4(\mu_3\text{-P})_4$ ⁴ and Ti_2P_6 ,⁵ complexes containing 'zigzag' P chains,⁶ η^5 - P_5 and η^6 - P_6 rings,^{1,7,8} and encapsulated μ_6 -, μ_9 - and μ_{10} -P atoms.¹ We describe the isolation of a new type of phosphidochromium cluster containing metal carbonyl fragments bonded to a polycyclic aggregate of ten P atoms.

The co-thermolysis of $[(\text{Cp})\text{Cr}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with yellow P_4 (1.5 mol equiv.) in toluene at 80–85 °C for 4 h gave a mixture of products, from which was isolated $(\text{Cp})_2\text{Cr}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)$ (34%), $(\text{Cp})_2\text{Cr}(\text{CO})_2(\eta^3\text{-P}_3)$ (34%), $(\text{Cp})_2\text{Cr}_2(\text{CO})_4$ (17%) and $[(\text{Cp})\text{Cr}(\text{CO})_2]_5\text{P}_{10}$, **1**, (13%) by alumina column chromatography. Complex **1** was eluted with diethyl ether and obtained as an air-stable reddish-brown crystalline solid.† Diffraction-quality, chunky poly-faceted dark-brown crystals were obtained from benzene–tetrahydrofuran (THF) after 9 days at ambient temperature, and one of these was examined by single crystal X-ray diffraction to reveal the novel central P_{10} unit.‡

The structure consists of a central P_{10}Cr_5 unit with each metal atom joined to two P atoms, of which four bond to two metals, two bond to one, and the remaining four each bond to three other P atoms. Fig. 1 shows a stereoview of the Cr_5P_{10} unit. The atoms are numbered according to the chromium atoms such that Cr(1) through Cr(5) lie in a rough plane with Cr(1), Cr(3) and Cr(4) above and Cr(2) and Cr(5) slightly below the plane. The P–P distance (average 2.22 Å) is very

close to the value of 2.21 Å in P_4 vapour;¹¹ this is indicative of P–P single bonds throughout the P_{10} core. The Cr–P distance (average 2.43 Å) falls within the range observed for other $(\text{Cp})\text{Cr}(\text{CO})_2$ complexes, viz. 2.341–2.474 Å for $[(\text{Cp})\text{Cr}(\text{CO})_2]_2(\mu\text{-}\eta^2\text{-P}_2)$ and (2.427–2.494 Å) for $(\text{Cp})\text{Cr}(\text{CO})_2(\eta^3\text{-P}_3)$.¹²

The P_{10} unit makes up a unique polyphosphorus structure. Two six-membered rings (boat configuration) of distorted sp^3 trigonal P atoms share the P(8)–P(1)–P(9) fragment, with an external link P(4)–P(7), and a single external ring substituent, P(3). The ring system can also be described in terms of the three cyclopentane-type rings with P(4)–P(9) and P(7)–P(8) each shared by two rings and P(4)–P(7) shared by all three.

The three chromium atoms [Cr(1), Cr(2), Cr(3)], which form corner-sharing Cr–P₃ rings, produce a short P–P distance across these rings (2.80–2.85 Å) and a dramatically reduced P–P–P angle (79°) opposite the metal. Cr(4) links a larger P–P gap (3.042 Å) to make CrP_4 the smallest new ring. Cr(5) bonds across the P(5)–P(6) bond to form a three-membered ring.

Despite the syntheses of many polycyclophosphanes in the last two decades,¹³ bonding of these homocyclic annelated ring systems to organometallic fragments was previously unknown. The structure of **1** contains three homocyclic P₅ rings annelated as in the polyanion¹⁴ P_{16}^{2-} and heterocyclic rings, which include one three-membered CrP_2 , three four-membered CrP_3 , one five-membered CrP_4 , four six-membered CrP_5 , and one six-membered Cr_2P_4 , with each of the five $(\text{Cp})\text{Cr}(\text{CO})_2$ fragments bridging across two P atoms. Known mono-metal polyphosphides are reported to contain only a simple monocyclic phosphane, e.g. cyclic P_6 in Ti_2P_6 ⁵ and Th_2P_{11} .¹⁵ In the bimetallic phosphide $\text{Cu}_4\text{SnP}_{10}$, the only other example of a M_5P_{10} complex, a quasi-tetrahedral $[\text{SnCu}_3]$ -cluster inter-links four adamantane P_{10}^{6-} groups,

† Satisfactory elemental analysis. IR (THF): ν_{CO} 1925 vs. 1855 s. ¹H NMR (C_6D_6) δ (CP) 5.07, 4.90, 4.51, 4.43, 4.35, indicating five inequivalent (Cp) rings; ¹³C NMR δ (Cp) 89.72–88.82 (cluster of 4–5 unresolved peaks). MS (parent ion not observed) m/z : unassigned peaks at 469 and 431, 389 $[(\text{Cp})_2\text{Cr}_2\text{P}_5]$, 358 $[(\text{Cp})_2\text{Cr}_2\text{P}_4]$, 327 $[(\text{Cp})_2\text{Cr}_2\text{P}_3]$, 296 $[(\text{Cp})_2\text{Cr}_2\text{P}_2]$, 266 $[(\text{Cp})_2\text{Cr}(\text{CO})_2\text{P}_3]$, 262 $[(\text{Cp})_2\text{Cr}_2\text{P}_3]$, 238 $[(\text{Cp})\text{Cr}(\text{CO})\text{P}_3]$, 213 $[(\text{Cp})_2\text{CrP}]$, 210 $[(\text{Cp})\text{CrP}_3]$, 200 $[(\text{Cp})\text{Cr}_2\text{P}]$, 182 $[(\text{Cp})_2\text{Cr}]$, 169 $[(\text{Cp})\text{Cr}_2]$. ESR in toluene at ambient temperature—1:2:1 triplet (g 2.0086, splitting 28.3 G). Magnetic moment 1.75 J T⁻¹ (1 J T⁻¹ = 1 Bohr magneton).

‡ Crystal data for **1**: space group $\text{P}\bar{1}$ with $Z = 2$, $a = 12.339(3)$, $b = 13.993(3)$, $c = 16.115(6)$ Å; $\alpha = 94.52(2)$, $\beta = 92.93(4)$, $\gamma = 114.20(3)^\circ$. Data were collected as previously described¹⁸ on an Enraf-Nonius CAD4 four-circle graphite-monochromated diffractometer. 6884 reflections had $F_o^2 > 3 \sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.^{9,10} Lorentz-polarization and absorption corrections were applied, based on the solved structure and indexed crystal faces.^{18,19} The positions of the metal and phosphorus atoms were determined from three-dimensional Patterson functions. Other atoms were located from Fourier difference syntheses. Full-matrix least-squares refinement was carried out using the TEXRAY program set. $R = 6.1\%$ and $R_w = 7.2\%$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

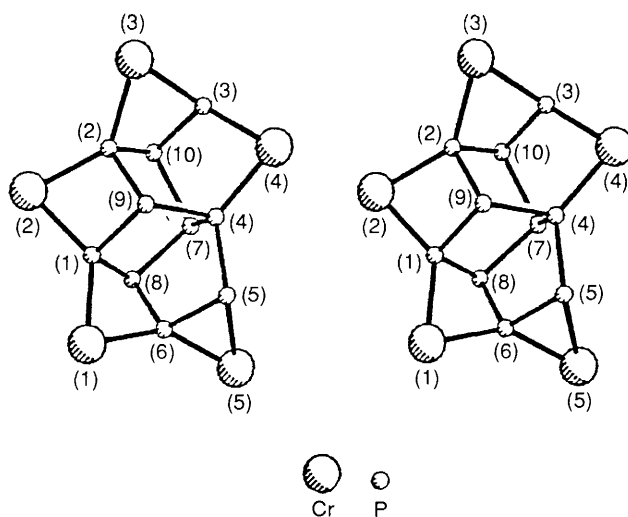


Fig. 1 Stereoview of the Cr_5P_{10} unit; CO and (Cp) groups removed for clarity

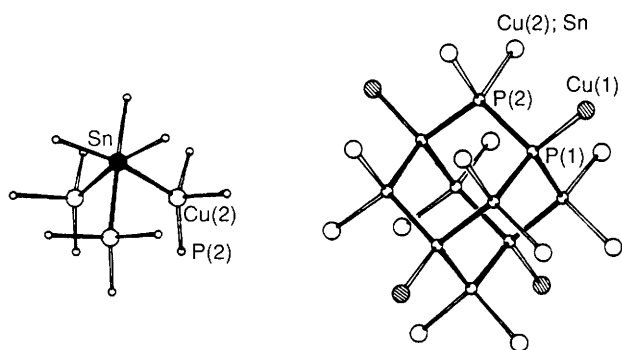


Fig. 2 Left: [SnCu₃]-cluster in the polyphosphide Cu₄SnP₁₀. Right: P₁₀⁶⁻ skeleton together with bonded Cu and Sn atoms

thereby forming an extended structure containing six trimetallic six-membered rings as well as six bimetallic five-membered rings, all centred at Sn, as shown in Fig. 2.¹⁶ It is apparent that there exists no similarity with the structure of 1, wherein five [(Cp)Cr(CO)₂] fragments on the periphery of a P₁₀ core form a discrete entity.

If a neutral core is considered, the formal oxidation state of each Cr is +1. The molecule possesses a valence-electron count of 125, 15e per (Cp)Cr(CO)₂ fragment and 5e per P atom. One way of rationalising the bonding in this complex is to assume that each P atom forms only single bonds to other P atoms, so that each has three 'single' electrons and one 'lone pair', potentially available for bonding to Cr atoms. Certain P atoms connect to three other atoms [P(3), P(5), P(7), P(8), P(9), P(10)] and the remaining P atoms [P(1), P(2), P(4) and P(6)] connect to four other atoms. Thus, each 3-connected P atom uses only its three single electrons for bonding to other P atoms, and retains a lone pair, while the 4-connected P-atoms each use all five available electrons for bonding. For instance, P(1) forms three two-centre two-electron bonds with Cr(1), P(8) and P(9) and donates two electrons to Cr(2) forming a coordinate bond. Applying this procedure from P(1) to P(6) indicates that the Cr atoms 1-4 are each 18e centres, whereas Cr(5) is the unique 17e centre joined to two P atoms, consistent with the observed 1:2:1 triplet signal in the ESR spectrum. The *g* value 2.0086 (splitting 28.3 G) is characteristic of an electron centred on Cr, with hyperfine coupling to two P atoms.¹⁷ It is unusual that the odd electron is hardly felt by the (Cp) rings, since these show up as sharp peaks in the NMR spectrum, with chemical shifts characteristic for dia-

magnetic (Cp) resonances. These observations are under further investigation.

Support from NSF grants CHE-8300516 and CHE-8609272, IRPA grant 04-07-04-127 and the University of Malaya are gratefully acknowledged. Special thanks are also due to Professor N. N. Greenwood for helpful discussions and to Dr Y. Y. Lim for the ESR spectrum.

Received, 4th June 1990; Com. 0/02497J

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