

# Novel Polycyclic Phosphane-to-Metal Coordination. Reaction of $[\text{CpCr}(\text{CO})_3]_2$ with Elemental Phosphorus and Structure and Paramagnetism of the Odd-Electron Complex $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$

Lai Yoong Goh,<sup>\*1a</sup> Richard C. S. Wong,<sup>1a</sup> and Ekkehard Sinn<sup>\*1b</sup>

Departments of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia, and  
University of Hull, Hull HU6 7RX, U.K.

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The cothermolysis of  $[\text{CpCr}(\text{CO})_3]_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$  with 1.5 mol equiv of  $\text{P}_4$  at 85 °C for 4 h resulted in the isolation of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)$  (2),  $\text{CpCr}(\text{CO})_2(\eta^3\text{-P}_3)$  (3),  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  (4), and  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5) in 34, 34, 17, and 13% yields, respectively. The reaction of 4 with  $\text{P}_4$  for 1.5 h, gave a similar mixture of 2, 3, and 5. The structure of the  $\text{P}_{10}$  unit in 5 is unique in polyphosphane chemistry. Its novel mode of coordination to organotransition metal groups is the first known instance of its kind. A further unusual feature is that 5 forms an odd-electron molecule, which is therefore paramagnetic; the 35-GHz EPR spectrum of an arbitrarily oriented single crystal at 6.1 K shows a complex 30-peak signal. The magnetic moment is 1.75  $\mu_B$ . The NMR spectrum shows that delocalization of unpaired spin density onto the Cp ligands is negligible. The complex undergoes three one-electron processes at 200 K: a quasi-reversible reduction at -1.29 V and two reversible oxidations at 0.61 and 1.03 V, respectively. 5 crystallizes as dark brown chunky polyhedra; crystal data: space group  $\text{P}\bar{1}$  with  $Z = 2$ ,  $a = 12.339$  (3) Å,  $b = 13.993$  (3) Å,  $c = 16.115$  (6) Å,  $\alpha = 94.52$  (2)°,  $\beta = 92.93$  (4)°,  $\gamma = 114.20$  (3)°.  $R = 6.1\%$  for 6884 reflections.

## Introduction

Prior to our preliminary report of the title complex (5),<sup>2</sup> the coordination of polycyclophosphanes to metal atoms was unknown. This was soon followed by Dahl's synthesis of two Fe complexes containing the cage-like  $\text{P}_8$  subunit of Hittorf's monoclinic phosphorus allotrope.<sup>3</sup> The complex (5) has been synthesized by taking advantage of the reactivity of the M-M bond in the dimer  $[\text{CpCr}(\text{CO})_3]_2$  (1).<sup>4-6</sup> Recent work on its reactions with the elemental chalcogens has led to the generation of some new dichromium complexes of S and Se.<sup>7,8</sup> The study of this reactivity with the non-metals was recently extended to elemental  $\text{P}_4$  and has led to the isolation of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-P}_2)$  (2) and  $\text{CpCr}(\text{CO})_2(\eta^3\text{-P}_3)$  (3) in substantially better yields than those reported for the analogous  $\mu\text{-}\eta^2\text{-P}_2$  and  $\eta^3\text{-P}_3$  complexes obtained from the reaction of  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Cr, Mo, W}$  and  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$  or  $\eta^5\text{-C}_5\text{Me}_5$ ) with elemental  $\text{P}_4$ .<sup>10-12</sup> We present here the results of further investigations which led to the isolation of additional products,

$\text{Cp}_2\text{Cr}_2(\text{CO})_4$  (4) and  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5), together with an X-ray structural analysis of 5. Also described is a small-scale reaction of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  (4) to give good yields of 2 and 3, along with a minor amount of 5.

## Experimental Section

**General Comments.** All reactions were carried out either by using conventional Schlenk techniques under a nitrogen atmosphere or in an argon atmosphere in a Vacuum Atmospheres drier equipped with a Model HE493 dri-train.

**Reagents and Solvents.** Yellow phosphorus was used as supplied by BDH Chemicals Ltd., without further purification.  $[\text{CpCr}(\text{CO})_3]_2$  was synthesized from  $\text{Cr}(\text{CO})_6$  (Aldrich Chemical Co.) as described by Manning.<sup>13</sup> All solvents used were dried over sodium benzophenone and distilled before use. Alumina was dried at 14 °C overnight before chromatographic use.

**Physical Measurements and Elemental Analyses.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL FX100 spectrometer, and chemical shifts referenced to residual  $\text{C}_6\text{H}_6$  in benzene- $d_6$  or to  $(\text{CH}_3)_4\text{Si}$  in toluene- $d_8$ .  $^{31}\text{P}$  spectra were measured on the JEOL FX90Q FT, 36.23-MHz spectrometer and chemical shifts referenced to external  $\text{H}_3\text{PO}_4$ . IR spectra were measured in the range 4000-200  $\text{cm}^{-1}$  by means of a Perkin-Elmer 1330 instrument. The EI mass spectra were run on a Kratos AEI MS 3074 spectrometer. Magnetic moment measurements were made on an SHE SQUID magnetometer and corrected for diamagnetism using Pascal's constants.<sup>14</sup> Calibration and operation of this instrument were described elsewhere.<sup>15,16</sup> EPR spectra were run

(1) (a) University of Malaya. (b) University of Hull.  
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Table I. Product Composition from the Reaction of  $[\text{CpCr}(\text{CO})_3]_2$  (1) with Various Mole Equivalents of  $\text{P}_4$ <sup>a</sup>

Cr:P (mole)	reaction time (h)	products (% yields)				
		$\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{P}_2$ (2)	$\text{CpCr}(\text{CO})_2\text{P}_3$ (3)	$\text{Cp}_2\text{Cr}_2(\text{CO})_4$ (4)	$[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$ (5)	others
1:1	3.5 <sup>b</sup>	36	42	12	0	10 (unidentified $\delta$ 4.03)
	3.5 <sup>c,d</sup>	19	14	16	6	
1:2	3.5 <sup>d,e</sup>	53	40	0	0	
	1.25 <sup>b</sup>	37	23	17	0	24 (unidentified $\delta$ 4.48 br) <sup>f</sup>
1:3	4 <sup>f,d</sup>	34	34	17	13	
1:4	3.5 <sup>b,g</sup>	37	45	0	18	
	10 <sup>b,g</sup>	12	50	0	14	24 ( $\text{Cp}_2\text{Cr}_2\text{P}_5$ ) <sup>h</sup>
	15 <sup>b,g</sup>	2	33	0	22	43 ( $\text{Cp}_2\text{Cr}_2\text{P}_5$ ) <sup>h</sup>

<sup>a</sup> In toluene, at 90 °C, unless otherwise stated. <sup>b</sup> Product yields by integration of Cp resonances in <sup>1</sup>H NMR spectrum of product mixture. <sup>c</sup> At 110 °C. <sup>d</sup> Product yields of isolated complexes. <sup>e</sup> From ref 9. <sup>f</sup> At 80–85 °C. <sup>g</sup> Aliquots of the same reaction mixture. <sup>h</sup> From ref 18. <sup>i</sup> br = broad.

on a Varian V4502 spectrometer with a 35-GHz bridge (Model V-4561). Sample temperature measurement and control were achieved with the normal Varian cavity adapted to fit an Oxford Instruments ESR9 flow cryostat and Model ITC4 temperature controller. Cyclic voltammograms were obtained with a Princeton Applied Research 170 potentiostat. Electrochemical measurements were carried out under a dry nitrogen atmosphere in freshly distilled  $\text{CH}_2\text{Cl}_2$  containing 0.5 M (*n*-Bu<sub>4</sub>N)PF<sub>6</sub> using a Pt working electrode vs Ag/AgCl.

Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University.

**Reactions of  $[\text{CpCr}(\text{CO})_3]_2$  with  $\text{P}_4$ .** (a) **Isolation of  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5) from 1:3 Cr:P Mole Ratio.** A deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (200 mg, 0.50 mmol) and yellow  $\text{P}_4$  (93 mg, 0.75 mmol) in toluene (ca. 20 mL) was stirred at 80–85 °C for ca. 4 h. The resultant reddish brown solution was filtered through a 2-cm disk of Celite and the filtrate concentrated to ca. 1 mL. This was loaded onto an alumina column (1.5 × 11 cm) prepared in *n*-hexane. Elution gave four fractions: (i) a yellow fraction in *n*-hexane (15 mL) which yielded yellowish brown flakes of  $\text{CpCr}(\text{CO})_2\text{P}_3$  (3) (90 mg, 0.34 mmol, 34%) (<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$ (Cp) 3.92<sup>g</sup>); (ii) a green fraction in *n*-hexane (20 mL) which yielded dark green solids of  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  (4) (30 mg, 0.087 mmol, 17%), characterized by its elemental analysis (Anal. Calcd for  $[\text{C}_7\text{H}_5\text{CrO}_2]_2$ : C, 48.55; H, 2.89; Cr, 30.05. Found: C, 48.64; H, 2.95; Cr, 30.38), its mp (205–206 °C, [reported:<sup>4</sup> 205–206 °C]), its IR data ( $\nu(\text{CO})$  1904 (vs), 1881  $\text{cm}^{-1}$  (vs) ( $\text{C}_6\text{D}_6$ ) [reported:<sup>4</sup>  $\nu(\text{CO})$  1904, 1881  $\text{cm}^{-1}$  ( $\text{CS}_2$ )]), and its <sup>1</sup>H NMR ((benzene-*d*<sub>6</sub>):  $\delta$ (Cp) 4.23) and MS data (*m/z* 346 ( $\text{Cp}_2\text{Cr}_2(\text{CO})_4$ ), 318 ( $\text{Cp}_2\text{Cr}_2(\text{CO})_3$ ), 290 ( $\text{Cp}_2\text{Cr}_2(\text{CO})_2$ ), 262 ( $\text{Cp}_2\text{Cr}_2(\text{CO})$ ), 234 ( $\text{Cp}_2\text{Cr}_2$ ), 201 ( $\text{CpCr}(\text{CO})_3$ ), 182 ( $\text{Cp}_2\text{Cr}$ ), 173 ( $\text{CpCr}(\text{CO})_2$ ), 145 ( $\text{CpCr}(\text{CO})$ ), and 117 ( $\text{CpCr}$ )); (iii) a magenta fraction in 1:1 *n*-hexane-toluene (20 mL) plus toluene (10 mL) which gave  $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{P}_2$  (2) (70 mg, 0.17 mmol, 34%) (<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$ (Cp) 4.15<sup>g</sup>); (iv) a reddish brown fraction in 1:1 ether-toluene (20 mL) and ether (10 mL) which yielded, after crystallization from benzene, fine crystalline reddish brown needles of  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5) (30 mg, 0.026 mmol, 13%). For 5: <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$ (Cp) 5.07, 4.90, 4.51, 4.43, 4.35; <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>):  $\delta$ (Cp) 5.06, 4.90, 4.50 (relative intensity 1:1:3); <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>):  $\delta$ (Cp) 89.72–88.82 (unresolved cluster of 4–5 peaks); IR  $\nu(\text{CO})$  1925 (vs) 1855  $\text{cm}^{-1}$  (s) (THF); FAB<sup>+</sup>-MS *m/z* 1175.6 ( $\text{Cp}_5\text{Cr}_5(\text{CO})_{10}\text{P}_{10}$ ), 1119.6 ( $\text{Cp}_5\text{Cr}_5(\text{CO})_8\text{P}_{10}$ ), and 1063 ( $\text{Cp}_5\text{Cr}_5(\text{CO})_6\text{P}_{10}$ ); EI-MS *m/z* (parent ion not observed) 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 ( $\text{CpCr}(\text{CO})_2\text{P}_3$ ), 262 ( $\text{CpCr}_2\text{P}_3$ ), 238 ( $\text{CpCr}(\text{CO})\text{P}_3$ ), 213 ( $\text{Cp}_2\text{CrP}$ ), 210 ( $\text{CpCrP}_3$ ), 200 ( $\text{CpCr}_2\text{P}$ ), 182 ( $\text{Cp}_2\text{Cr}$ ), and 169 ( $\text{CpCr}$ ). Anal. Calcd for  $[\text{C}_7\text{H}_5\text{CrO}_2\text{P}_2]_5\text{C}_6\text{H}_6$ : C, 39.27; H, 2.47; P, 24.74. Found: C, 40.12; H, 2.57; P, 24.0. Sample reanalysis after standing, Anal. Calcd for  $[\text{C}_7\text{H}_5\text{CrO}_2\text{P}_2]_5\text{C}_6\text{H}_6$ : C, 37.56; H, 2.31. Found: C, 37.40, 37.04; H, 2.42, 2.49. The presence of  $\text{C}_6\text{H}_6$  in the molecule was detected in its proton NMR spectrum in  $\text{CD}_2\text{Cl}_2$ .

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(b) **Isolation of  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5) from 1:1 Cr:P Ratio.** A similar reaction of  $[\text{CpCr}(\text{CO})_3]_2$  (500 mg, 1.24 mmol) with  $\text{P}_4$  (77 mg, 0.62 mmol) in toluene (ca. 30 mL) was carried out at gentle reflux for 3.5 h, and the products isolated as described above are given in Table I.

**NMR Experiments. Estimation of Product Yields.** A typical reaction was as follows: for a Cr:P ratio of 1:1, a deep green suspension of  $[\text{CpCr}(\text{CO})_3]_2$  (50 mg, 0.124 mmol) and  $\text{P}_4$  (7.7 mg, 0.062 mmol) in toluene (ca. 3 mL) was magnetically stirred in a Schlenk flask equipped with a condenser and immersed in an oil bath maintained at ca. 90 °C. An aliquot (0.5–1.0 mL) was syringe-transferred to another flask at intervals, evacuated to dryness, and totally redissolved in  $\text{C}_6\text{D}_6$  for a <sup>1</sup>H NMR spectral scan. The product composition and yields, as estimated from integrals of the Cp resonances, are given in Table I for Cr:P mole equivalents of 1:1, 1:2, and 1:4.

**Thermal Decarbonylation of  $[\text{CpCr}(\text{CO})_3]_2$  (1) to  $[\text{CpCr}(\text{CO})_2]_2$  (4).** A solution of  $[\text{CpCr}(\text{CO})_3]_2$  (10 mg, 0.025 mmol) in toluene-*d*<sub>8</sub> (0.5 mL) in a serum-capped 5-mm NMR tube, vented via a syringe needle into a nitrogen line, was maintained at 85 °C. Its <sup>1</sup>H NMR spectrum, monitored at intervals, showed a slow conversion to 4 ( $\delta$  4.23) as follows: 0.5 h (5%), 1 h (14%), 2 h (18%), 4 h (26%). A similar rate of decarbonylation was observed for a stirred solution in a Schlenk flask under similar conditions.

In a similar experiment, a solution of 1 was totally converted to 4 after 3.75 h at 110 °C.

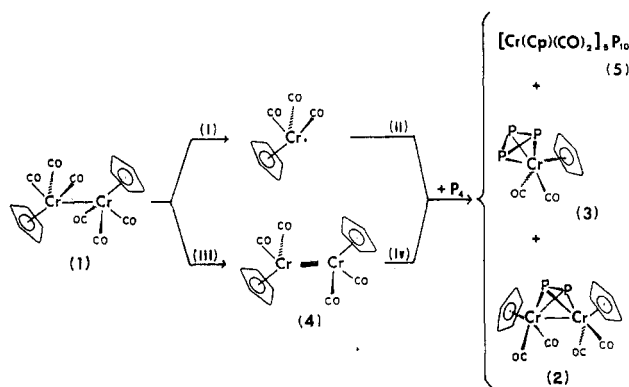
**Small-Scale Reaction of  $[\text{CpCr}(\text{CO})_2]_2$  (4) with  $\text{P}_4$ .** To a solution of 4, prepared as described above from 1 (10 mg, 0.025 mmol) in toluene-*d*<sub>8</sub> (0.7 mL), was added  $\text{P}_4$  (4.6 mg, 0.037 mmol). The mixture was agitated under ultrasound to achieve homogeneity and then maintained at 85 °C as above. Its <sup>1</sup>H NMR spectrum scanned at 0.5 and 1.5 h showed the formation of the following compounds: at 0.5 h, unresolved resonances of 4 and 2, 94%, and resonances of 3, 6%, and at 1.5 h, unresolved resonances of 4 and 5, 13%, resonances of 2, 50%, and 3, 37%, and an unidentified resonance at  $\delta$  5.68, 1–2%, and  $\text{Cp}_2\text{Cr}_2\text{P}_5$   $\delta$  18.8, trace. A chromatographic separation after 1.75 h on alumina (column 0.6 × 4.5 cm) gave (i) a yellow fraction in hexane, which yielded 3, contaminated with a trace of  $\text{Cp}_2\text{Cr}_2\text{P}_5$  (5.2 mg, 39% yield), (ii) a magenta fraction in toluene, which yielded 2 (3.1 mg, 30% yield), and (iii) a brown fraction in toluene-ether which yielded 5 (2.2 mg, 11% yield).

**Crystal Structure Analysis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_5\text{P}_{10}$  (5).** This complex was obtained as an air-stable reddish brown crystalline solid, and diffraction-quality, chunky polyfaceted dark brown crystals were obtained from benzene-THF after 9 days at ambient temperature. A single crystal 0.8 × 0.54 × 0.38 mm was selected for single-crystal X-ray examination.

**Crystal Data:** Space group  $\text{P}\bar{1}$  with  $Z = 2$ ,  $a = 12.339$  (3) Å,  $b = 13.993$  (3) Å,  $c = 16.115$  (6) Å,  $\alpha = 94.54$  (2)°,  $\beta = 92.93$  (4)°,  $\gamma = 114.20$  (3)°. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 13039 independent intensities, there were 6884 with  $F_o^2 > 3.00\sigma(F_o^2)$ , where  $\sigma(F_o^2)$  was estimated from counting statistics.<sup>17,18</sup>

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Scheme I



The positions of the metal and four of the phosphorus atoms were determined from Multan tangent functions. The intensity data were phased sufficiently well by these potential coordinates to permit location of the other non-hydrogen atoms from Fourier difference syntheses. Full-matrix least-squares refinement was carried out using the TEXRAY program set.

Data on a poorer crystal provided evidence of a positionally disordered benzene molecule (partial occupancy) near the cell centroid. Thereafter, microanalyses were performed on freshly prepared sample, which showed time-dependent loss of benzene. The good crystal, on which the parameters are based, had already lost benzene solvent without destruction of its crystallinity. The model converged with  $R = 6.1\%$  and  $R_w = 7.2\%$ . Final Fourier difference functions showed no peaks higher than  $0.93 \text{ e}/\text{\AA}^3$ .

## Results and Discussion

**Products and Reaction Pathways.** An earlier report<sup>9</sup> described the isolation of  $[\text{CpCr}(\text{CO})_2]_2(\mu\text{-}\eta^2\text{-P}_2)$  (2) and  $\text{CpCr}(\text{CO})_2(\eta^3\text{-P}_3)$  (3) from the reaction of  $[\text{CpCr}(\text{CO})_3]_2$  with 1 mol equiv of  $\text{P}_4$  in 53 and 40% yields, respectively. Our present experiments via spectra detection and/or isolation of products show that the reaction produces a mixture of 2, 3,  $[\text{CpCr}(\text{CO})_2]_2$  (4), and  $[\text{CpCr}(\text{CO})_2]_2\text{P}_{10}$  (5), the relative composition of which varies with both the Cr:P mole ratio and the duration of reaction, as shown in Table I. Generally, complexes 2 and 3 account for more than 70% of the total product yield after 3.5 h. The Cr=Cr complex (4) was spectrally detected or isolated (a) at low P:Cr ratios, e.g. 1:1, despite a higher reaction temperature of  $110^\circ\text{C}$ , or (b) before completion of reaction, e.g. 1.25 h at  $90^\circ\text{C}$  or 4 h at  $80\text{--}85^\circ\text{C}$  for P:Cr ratios of 2:1 and 3:1, respectively. At the higher P:Cr ratio of 4:1, 4 was not detected at all. Instead, the polyphosphane complex, 5, was formed in substantial yield (ca. 20%). In addition, monitoring this reaction up to 15 h indicated that 5 was thermally stable, as was 3, while 2 completely degraded to  $\text{Cp}_2\text{Cr}_2\text{P}_5$  ( $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  18.8 ( $\nu_{1/2}$  ca. 100 Hz)).<sup>19</sup>

The detection and isolation of  $[\text{Cp}(\text{CO})_2\text{Cr}=\text{Cr}(\text{CO})_2\text{Cp}]$  (4) necessitated control experiments involving the thermal decarbonylation of 1 as well as the cothermolysis of 4 with  $\text{P}_4$  under similar reaction conditions, in order to diagnose the reaction pathways (Scheme I). Although Manning<sup>4</sup> had reported a facile thermal conversion (90%) of  $[\text{CpCr}(\text{CO})_3]_2$  to 4 after 2.5 h in refluxing toluene, NMR spectral monitoring showed that the decarbonylation process, route iii, was only 26% complete after 4 h at  $80\text{--}85^\circ\text{C}$ .

Considering that the reaction of  $[\text{CpCr}(\text{CO})_3]_2$  with  $\text{P}_4$  required only 4 h to reach completion under these conditions, these findings indicate that route iv, via 4, that Scherer had established for the  $(\text{C}_5\text{Me}_5)$  analogs of Cr, Mo, and W complexes,<sup>10–12</sup> can only constitute a subsidiary pathway. This indicates that our earlier proposed radical route,<sup>9</sup> shown as pathway ii, must be the predominant pathway, in agreement with the observed facile Cr—Cr bond dissociation<sup>15,6,20–22</sup> and accumulating evidence suggesting that reactions of 1 generally proceed via its 17-electron monomeric derivative.<sup>5,6</sup>

As shown in Table I, the polyphosphane complex 5 is only formed with P:Cr equivalents greater than or equal to 3:1 at  $90^\circ\text{C}$ , though at  $110^\circ\text{C}$ , a small amount (6%) is formed in a reaction using a P:Cr mole ratio of 1:1. The small-scale reaction of 4 at  $85^\circ\text{C}$ , using a P:Cr mole equivalent of 3:1, also produces 5 (11%). These findings, together with earlier reports,<sup>10–12</sup> indicate that the quantitative product distribution depends on detailed thermolysis conditions. A similar dependence was observed in the synthesis of polycyclic organophosphanes via the thermolysis of corresponding phosphorus-poorer smaller cyclic compounds.<sup>23,24</sup>

**Properties and Spectral Characteristics of 5.** The complex crystallizes as air-stable reddish brown needles, insoluble in *n*-hexane but moderately soluble in benzene, toluene, and THF to give brown solutions. A THF solution exhibits CO stretching frequencies at 1925 (vs) and 1855  $\text{cm}^{-1}$  (s). The FAB mass spectrum shows the parent ion  $m/z = 1175.6$  ( $\text{Cp}_5\text{Cr}_5(\text{CO})_{10}\text{P}_{10}$ ) and two other  $\text{P}_{10}$ -containing ions, viz.  $m/z$  1119.6 ( $\text{Cp}_5\text{Cr}_5(\text{CO})_8\text{P}_{10}$ ) and 1063 ( $\text{Cp}_5\text{Cr}_5(\text{CO})_6\text{P}_{10}$ ). In the EI mass spectrum, only mass fragments arising from  $\text{Cp}_2\text{Cr}_2\text{P}_5$  and  $\text{CpCr}(\text{CO})_2\text{P}_3$ <sup>9</sup> were observed. The proton NMR spectrum in benzene- $d_6$  shows five Cp resonances—two sharp peaks at  $\delta$  5.07 and 4.90 ( $\nu_{1/2}$  3 Hz) and three broader peaks at  $\delta$  4.51 ( $\nu_{1/2}$  6 Hz), 4.43 ( $\nu_{1/2}$  12 Hz), and 4.35 ( $\nu_{1/2}$  12 Hz). In toluene- $d_8$ , within the temperature range  $-50$  to  $+90^\circ\text{C}$ , the two sharp peaks exhibit little change in their line widths or chemical shifts, which vary from  $\delta$  5.00 to 5.05 (i.e.  $\Delta\delta = 0.05$ ) and  $\delta$  4.84 to 4.87 (i.e.  $\Delta\delta = 0.03$ ), respectively. The three broader resonances show greater VT behavior, their temperature-dependent shifts being more pronounced than for the above. Thus their chemical shifts for the temperature range  $-50$  to  $+90^\circ\text{C}$  are (i)  $\delta = 4.38\text{--}4.54$  (i.e.  $\Delta\delta = 0.16$ ) (ii)  $\delta = 4.28\text{--}4.46$  (i.e.  $\Delta\delta = 0.18$ ), and (iii)  $\delta = 4.18\text{--}4.44$  (i.e.  $\Delta\delta = 0.26$ ), respectively. Of these, the two higher-field resonances almost coalesce at  $0^\circ\text{C}$  to give a broad peak centered at  $\delta$  4.34. At  $-50$  and  $+90^\circ\text{C}$ , their line widths are all similar to those of the two sharp peaks at  $\delta$  5.00–5.05 and  $\delta$  4.84–4.87, respectively. The  $^{13}\text{C}$  NMR spectrum shows an unresolved cluster of 4–5 peaks at  $\delta$  89.72–89.82. The  $^{31}\text{P}$  NMR spectrum is illustrated in Figure 1. Owing to a lack of symmetry, 10 clusters of resonances are observed for the  $\text{P}_{10}$  core, with chemical shifts ranging between  $-170.5$  and  $+232.6$  ppm, as detailed in Table II. This span of chemical shifts is greater than any observed for Baudler's cyclic and polycyclic organophosphanes, of which  $\text{P}_9^t\text{Bu}_3$  and  $\text{P}_{16}^{2-}$  had been found to possess P resonances between  $-180$  and  $+150$  ppm<sup>23</sup>

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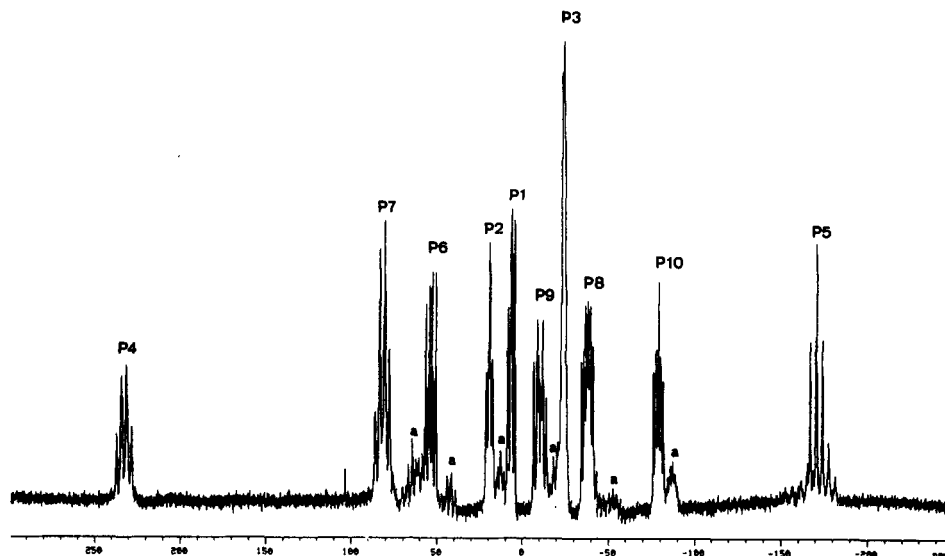


Figure 1.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{CpCr}(\text{CO})_2]_5\text{Pr}_{10}$  (5). <sup>a</sup>From unknown impurities.

Table II.  $^{31}\text{P}\{^1\text{H}\}$  NMR Resonances of 5

chemical shift ( $\pm 0.2$ ppm)	assgnt	multiplicity [ $J$ ( $\pm 20$ Hz)]	connectivities
+232.8	P4	ddd (430, 310, <sup>a</sup> 370 <sup>a</sup> )	P5P7P9Cr4
+82.0	P7	ddd (310, 370, <sup>a</sup> 340 <sup>a</sup> )	P4P8P10
+53.8	P6	dd (450, 260)	P5P8Cr1Cr5
+19.3	P2	dd (220, <sup>a</sup> 205)	P9P10Cr2Cr3
+6.5	P1	dd (270, 215)	P8P9Cr1Cr2
-10.3	P9	ddd (220, 270, 370)	P1P2P4
-23.9	P3	d (140)	P10Cr3Cr4
-37.8	P8	ddd (215, 260, 370)	P1P6P7
-78.7	P10	ddd (205, 140, 340)	P2P3P7
-170.4	P5	dd (430, 450 <sup>a</sup> )	P4P6Cr5

<sup>a</sup> Estimated from broad fine structure.

and between  $-180$  and  $+60$  ppm,<sup>24</sup> respectively. Indeed, the resonance at 232.6 ppm occurs at lower field than any observed for polycyclic phosphanes. This could arise from the large variation in ring size: from three-membered to six-membered rings in 5. It has been observed that the more the rings of a cyclopolyphosphane differ in size, the larger is the difference of the observed chemical shifts, with P resonances in three- or four-membered rings shifted to higher field.<sup>25</sup> Fortunately, under such circumstances, higher-order effects become negligible and this makes it possible to make some empirical assignments. On the basis of first-order P-P coupling effects and the observed multiplicity of the resonances, the P-P connectivities pertaining to each set of resonances can be worked out to give the assignments as illustrated in Table II. The highest field chemical shift thus assigned to P5 agrees with what is expected for a P atom in a three-membered ring.

The EPR signal of the complex in solution reported in our preliminary communication<sup>2</sup> could not be confirmed. A frozen glass of the complex at 4.9 K showed a broad featureless X-band signal in the  $g = 4$  region. The 35-GHz EPR spectrum of an arbitrarily oriented single crystal at 6.1 K is complex (see Figure 2). It comprises about 30 peaks in the 1.68-T range of the magnet, the narrowest having a peak to peak derivative line width of  $1.5 \times 10^{-3}$  T. The pattern is highly dependent on crystal orientation in the field, shows significant broadening at 20 K, and has all but disappeared at 50 K. The multiplicity of peaks

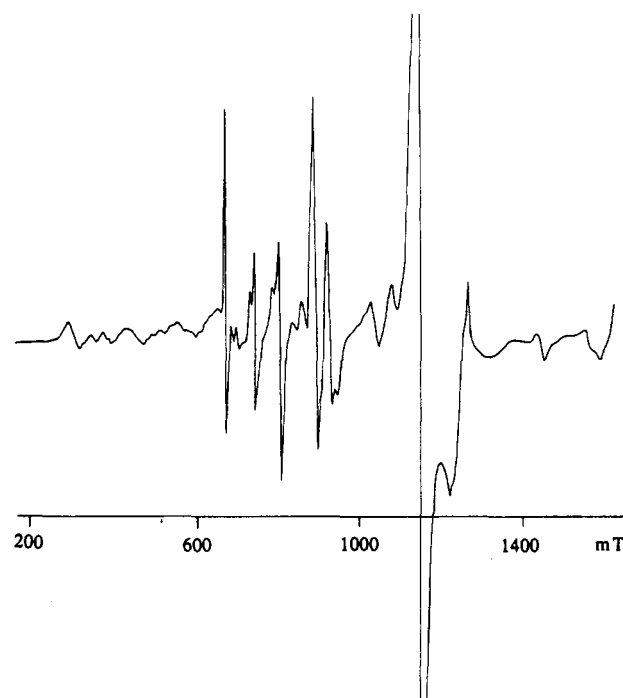


Figure 2. 35-GHz EPR spectrum of an arbitrarily oriented crystal of 5 at 6.1 K.

probably arises from a set of  $S = 1/2$  centers which are exchange coupled, but at this stage of our investigations other explanations may fit. The multiplicity does not arise from magnetic inequivalence since the space group is  $P\bar{1}$  and there are two equivalent molecules in the cell (related by inversion). The relative temperature independence of intensities between 6 and 20 K suggests that any exchange couplings are small (less than or equal to  $1 \text{ cm}^{-1}$ ). To analyze the spectrum further could require considerable more work, both experimentally and theoretically.

The magnetic moment of  $1.75 \mu_B$  (18 K) for the solid confirms the presence of an unpaired electron. However, the solution magnetic moment could not be determined by Evans' method<sup>26</sup> on account of the low limiting solubility of the complex.

**Electrochemical Analysis.** Whereas complexes 2 and 3 do not exhibit any electrochemistry within the observed

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Table III. Positional Parameters for  $P_{10}[CpCr(CO)_2]_5$ 

atom	x	y	z	atom	x	y	z
Cr1	0.8499 (2)	0.1023 (2)	0.0824 (1)	C2Cr4	0.530 (2)	0.355 (1)	0.495 (1)
Cr2	1.0951 (2)	0.4270 (1)	0.2028 (1)	C3Cr4	0.435 (1)	0.316 (1)	0.451 (1)
Cr3	0.9040 (2)	0.6069 (1)	0.3224 (1)	C4Cr4	0.408 (2)	0.210 (1)	0.412 (1)
Cr4	0.5701 (2)	0.3310 (2)	0.3676 (1)	C5Cr4	0.520 (2)	0.197 (1)	0.447 (1)
Cr5	0.5948 (2)	-0.0747 (1)	0.2613 (1)	C41	0.559 (1)	0.452 (1)	0.345 (1)
P1	0.9155 (3)	0.2621 (2)	0.1836 (2)	O42	0.426 (1)	0.2625 (9)	0.1997 (8)
P2	0.9396 (3)	0.4527 (2)	0.2765 (2)	O41	0.539 (1)	0.526 (1)	0.3328 (8)
P3	0.7787 (3)	0.4606 (2)	0.3949 (2)	C42	0.485 (1)	0.288 (1)	0.268 (1)
P4	0.6731 (3)	0.2428 (2)	0.2969 (2)	C1Cr5	0.426 (2)	-0.158 (1)	0.181 (1)
P5	0.5856 (3)	0.0895 (2)	0.2170 (2)	C2Cr5	0.415 (1)	-0.208 (1)	0.255 (1)
P6	0.7424 (3)	0.0615 (2)	0.2045 (2)	C3Cr5	0.501 (2)	-0.246 (1)	0.258 (1)
P7	0.8060 (3)	0.2273 (2)	0.3845 (2)	C4Cr5	0.563 (2)	-0.221 (2)	0.187 (1)
P8	0.8945 (3)	0.1693 (2)	0.2904 (2)	C5Cr5	0.517 (2)	-0.170 (2)	0.142 (1)
P9	0.7824 (3)	0.3289 (2)	0.1998 (2)	C51	0.729 (1)	-0.073 (1)	0.3194 (9)
P10	0.9183 (3)	0.3983 (2)	0.4025 (2)	O51	0.803 (1)	-0.0838 (8)	0.3564 (8)
C1Cr1	0.697 (2)	0.100 (2)	0.014 (1)	C52	0.570 (1)	-0.035 (1)	0.364 (1)
C2Cr1	0.709 (2)	0.013 (2)	-0.016 (1)	O52	0.566 (1)	-0.011 (1)	0.439 (1)
C3Cr1	0.836 (2)	0.067 (2)	-0.053 (1)	H1Cr1	0.6310	0.1016	0.0373
C4Cr1	0.857 (2)	0.158 (1)	-0.042 (1)	H2Cr1	0.6519	-0.0576	-0.0105
C5Cr1	0.785 (2)	0.177 (2)	-0.007 (1)	H3Cr1	0.8801	0.0325	-0.0682
C11	1.015 (1)	0.143 (1)	0.089 (1)	H4Cr1	0.9225	0.2086	-0.0672
O11	1.116 (1)	0.165 (1)	0.0933 (8)	H5Cr1	0.7976	0.2504	0.0127
C12	0.863 (1)	-0.015 (1)	0.109 (1)	H1Cr2	1.1461	0.2568	0.2516
O12	0.862 (1)	-0.098 (1)	0.122 (1)	H2Cr2	1.2607	0.3499	0.1489
C1Cr2	1.183 (1)	0.330 (1)	0.252 (1)	H3Cr2	1.3411	0.5523	0.1900
C2Cr2	1.246 (1)	0.380 (1)	0.196 (1)	H4Cr2	1.2540	0.5711	0.3242
C3Cr2	1.294 (2)	0.497 (1)	0.220 (1)	H5Cr2	1.1424	0.3926	0.3700
C4Cr2	1.244 (1)	0.507 (1)	0.293 (1)	H1Cr3	0.8836	0.5654	0.1441
C5Cr2	1.181 (1)	0.408 (1)	0.324 (1)	H2Cr3	0.6924	0.5211	0.2112
C21	1.076 (1)	0.404 (1)	0.093 (1)	H3Cr3	0.7214	0.6799	0.3163
O21	1.075 (1)	0.392 (1)	0.020 (1)	H4Cr3	0.9456	0.8166	0.3143
C22	1.113 (1)	0.551 (1)	0.167 (1)	H5Cr3	1.0364	0.7410	0.2059
O22	1.130 (1)	0.6334 (9)	0.1456 (8)	H1Cr4	0.6594	0.2983	0.5197
C1Cr3	0.873 (1)	0.612 (1)	0.188 (1)	H2Cr4	0.5759	0.4283	0.5237
C2Cr3	0.762 (1)	0.586 (1)	0.225 (1)	H3Cr4	0.3728	0.3434	0.4419
C3Cr3	0.780 (1)	0.673 (1)	0.282 (1)	H4Cr4	0.3429	0.1697	0.3804
C4Cr3	0.908 (1)	0.751 (1)	0.282 (1)	H5Cr4	0.5338	0.1370	0.4357
C5Cr3	0.959 (1)	0.710 (1)	0.223 (1)	H1Cr5	0.3756	-0.1292	0.1599
C31	1.062 (1)	0.650 (1)	0.3599 (9)	H2Cr5	0.3585	-0.2143	0.2925
O31	1.161 (1)	0.6840 (8)	0.3800 (7)	H3Cr5	0.5136	-0.2856	0.2994
C32	0.908 (1)	0.668 (1)	0.422 (1)	H4Cr5	0.6372	-0.2274	0.1759
O32	0.915 (1)	0.7111 (9)	0.4952 (8)	H5Cr5	0.5394	-0.1430	0.0925
C1Cr4	0.583 (1)	0.282 (1)	0.492 (1)				

range between +1.20 and -1.60 V vs. Ag/AgCl, complex 5 undergoes three one-electron processes at 200 K: a quasi-reversible reduction at -1.29 V (observable by ac voltammetry) and two reversible oxidations at 0.61 and 1.03 V, respectively. A sample oxidized with  $AgPF_6$  in  $CD_2Cl_2$  gave a red-brown solution which exhibited a broad featureless peak in the  $^1H$  NMR at  $\delta$  5.2-4.8. This reverted to the starting material within 1-2 h at ambient temperature [ $\delta$ (Cp) at 5.25, 5.04, 4.97, 4.82, and 4.76 in  $CD_2Cl_2$ ].

**Structure.** The molecular structures of 2 and 3 have been reported.<sup>9</sup> The structure of 5 is shown in Figure 3. It contains a central  $P_{10}$  unit with each metal atom joined to two P atoms, of which four bond to two metals, two bond to a single metal atom, and the remaining four bond only to other P atoms. Figure 4 shows a stereoview of  $Cr_5P_{10}$ . The atoms are numbered according to the chromium atoms such that Cr1 through Cr5 lie in a rough plane with Cr1, Cr3, and Cr4 above and Cr2 and Cr5 slightly below the plane. Atomic and thermal parameters are given in Table III. Bond lengths and angles are given in Table IV.

The  $P_{10}$  unit makes up a unique polyphosphorus structure. Two boat-configured six-membered rings of distorted  $sp^3$  trigonal P atoms share the P8-P1-P9 fragment, with an external link P4-P7 and a single external ring substituent P3. The ring system can also be described

in terms of the three cyclopentane-type rings with P4-P9 and P7-P8 each shared by two rings and P4-P7 shared by all three.

The three chromium atoms (Cr1, Cr2, Cr3), which form corner-sharing  $CrP_3$  rings, produce a short P-P distance across the rings (2.80-2.85 Å) and a dramatically reduced P-P-P angle (79°) opposite the metal. Cr4 links a larger P-P gap (3.042 Å) to make  $CrP_4$  the smallest new ring. Cr5 bonds across the P5-P6 bond to form a three-membered ring.

The three four-membered  $CrP_3$  rings are unique. In each case the metal is at a nonbonding distance from the P atom on the opposite side. This distance is shortest for Cr3 (Cr3-P10 = 3.348 Å) and Cr1 (Cr1-P8 = 3.363 Å) and longest for Cr2 (Cr2-P9 = 3.522 Å). For the five-membered ring, the nonbonding M-P distances are greater (Cr4-P7 = 3.755 Å, Cr4-P10 = 4.002 Å), as expected.

The average P-P bond length is 2.22 Å, throughout the  $P_{10}$  core, indicating that the P-P bonds are single, close to the interatomic distance (2.21 Å) in  $P_4$  vapor.<sup>27</sup> The average Cr-P distance, 2.43 Å, falls within the range observed for other  $CpCr(CO)_2$  complexes, viz. 2.341-2.474 Å for  $[CpCr(CO)_2]_2(\mu-\eta^2-P_2)$  and 2.427-2.494 Å for  $[CpCr(CO)_2]_2(\eta^3-P_3)$ .<sup>9</sup>

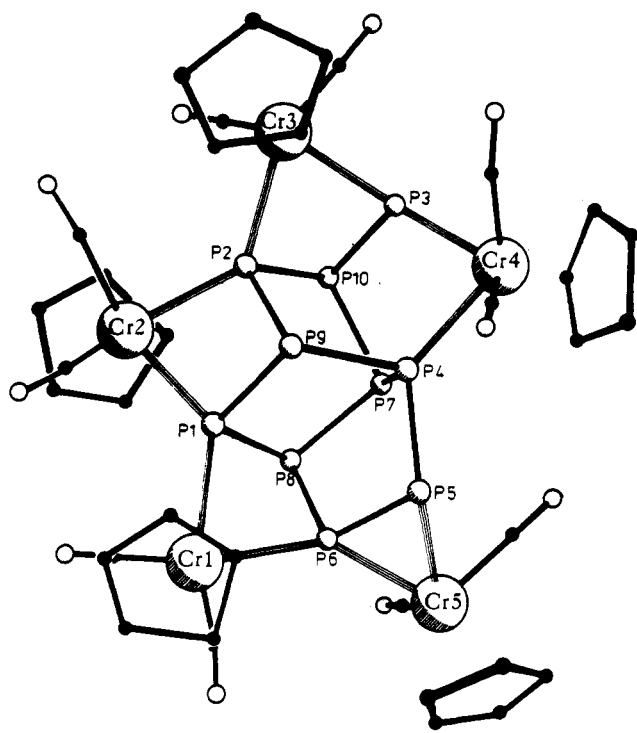


Figure 3. Structure of  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$  (5).

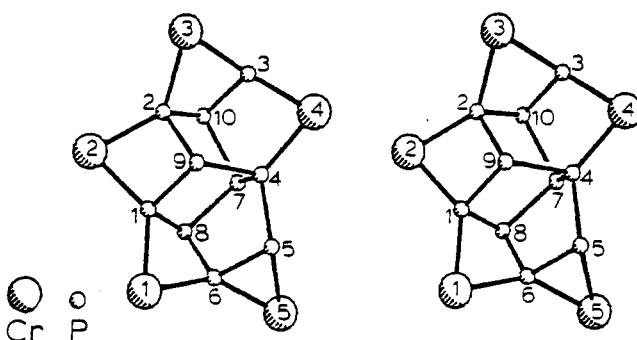


Figure 4. Stereoview of the  $\text{Cr}_5\text{P}_{10}$  unit of 5. CO and Cp groups are removed for clarity.

Despite the syntheses of many polycyclophosphanes in the last two decades,<sup>24,28</sup> the bonding of such homocyclic annelated ring systems to organometallic fragments was previously unknown. The structure of 1 contains three homocyclic  $\text{P}_5$  rings annelated like in the polyanion  $\text{P}_{16}^{2-}$ <sup>28</sup> and heterocyclic rings, which include one three-membered  $\text{CrP}_2$ , three four-membered  $\text{CrP}_3$ , one five-membered  $\text{CrP}_4$ , four six-membered  $\text{CrP}_5$ , and one six-membered  $\text{Cr}_2\text{P}_4$ , with each of the five  $\text{CpCr}(\text{CO})_2$  fragments bridging across two P atoms. The closest examples are the iron complexes  $\text{Cp}'_4\text{Fe}_4(\text{CO})_6\text{P}_8$  and  $\text{Cp}'_4\text{Fe}_6(\text{CO})_{13}\text{P}_8$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$ ) containing a regular-type  $\alpha\text{-P}_8$  core, wherein the coordination of the four bridgehead P atoms of the  $\text{P}_8$  subunit of Hittorf's monoclinic phosphorus to  $\text{Cp}'/\text{Fe}(\text{CO})_n$  fragments produces two four-membered  $\text{FeP}_3$  rings in both complexes and an additional five-membered  $\text{Fe}_2\text{P}_3$  ring in the second case.<sup>3</sup> The next nearest example involves the coordination of the P atoms of the cyclotriphosphane ring in the heptahetero-nortricyclene,  $\text{P}_4[\text{SiMe}_2]_3$  to  $\text{ML}_n$  fragments,<sup>29,30</sup> and other known metal polyphosphides

Table IV. Selected Bond Lengths and Angles for  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$

(a) Distances (Å)			
Cr1-C12	1.80 (2)	Cr4-C3Cr4	2.15 (2)
Cr1-C11	1.87 (2)	Cr4-C2Cr4	2.16 (2)
Cr1-C1Cr1	2.12 (2)	Cr4-C1Cr4	2.19 (2)
Cr1-C5Cr1	2.15 (2)	Cr4-C4Cr4	2.22 (2)
Cr1-C2Cr1	2.17 (2)	Cr4-C5Cr4	2.25 (2)
Cr1-C3Cr1	2.18 (2)	Cr4-P4	2.376 (4)
Cr1-C4Cr1	2.21 (2)	Cr4-P3	2.457 (4)
Cr1-P6	2.404 (4)	Cr5-C52	1.78 (1)
Cr1-P1	2.474 (4)	Cr5-C51	1.85 (1)
Cr2-C21	1.76 (2)	Cr5-C4Cr5	2.17 (2)
Cr2-C22	1.80 (2)	Cr5-C5Cr5	2.19 (2)
Cr2-C4Cr2	2.13 (2)	Cr5-C3Cr5	2.19 (2)
Cr2-C1Cr2	2.22 (2)	Cr5-C1Cr5	2.20 (2)
Cr2-C2Cr2	2.23 (2)	Cr5-C2Cr5	2.22 (2)
Cr2-C3Cr2	2.23 (2)	Cr5-P6	2.321 (4)
Cr2-C5Cr2	2.26 (2)	Cr5-P5	2.504 (4)
Cr2-P2	2.440 (4)	P1-P8	2.200 (5)
Cr2-P1	2.440 (4)	P1-P9	2.216 (5)
Cr3-C32	1.75 (2)	P2-P10	2.215 (5)
Cr3-C31	1.84 (1)	P2-P9	2.227 (4)
Cr3-C4Cr3	2.16 (1)	P3-P10	2.229 (5)
Cr3-C3Cr3	2.18 (2)	P4-P7	2.198 (5)
Cr3-C1Cr3	2.19 (2)	P4-P9	2.213 (5)
Cr3-C5Cr3	2.19 (2)	P4-P5	2.224 (4)
Cr3-C2Cr3	2.20 (2)	P5-P6	2.142 (5)
Cr3-P3	2.431 (4)	P6-P8	2.190 (5)
Cr3-P2	2.441 (4)	P7-P8	2.203 (5)
Cr4-C42	1.79 (2)	P7-P10	2.205 (4)
Cr4-C41	1.81 (2)		

(b) Angles (deg)

P6-Cr1-P1	70.1 (1)	P10-P3-Cr3	91.7 (2)
P2-Cr2-P1	71.5 (1)	P10-P3-Cr4	117.2 (2)
P3-Cr3-P2	71.6 (1)	Cr3-P3-Cr4	133.1 (2)
P4-Cr4-P3	78.0 (1)	P7-P4-P9	102.8 (2)
P6-Cr5-P5	52.5 (1)	P7-P4-P5	106.3 (2)
P8-P1-P9	102.6 (2)	P7-P4-Cr4	110.2 (2)
P8-P1-Cr2	112.9 (2)	P9-P4-P5	95.2 (2)
P8-P6-Cr1	94.0 (2)	P9-P4-Cr4	114.7 (2)
Cr5-P6-Cr1	142.4 (2)	P5-P4-Cr4	124.8 (2)
P4-P7-P8	96.9 (2)	P6-P5-P4	97.0 (2)
P4-P7-P10	93.4 (2)	P6-P5-Cr5	59.3 (1)
P8-P7-P10	102.9 (2)	P4-P5-Cr5	121.5 (2)
P6-P8-P1	79.4 (2)	P5-P6-P8	112.8 (2)
P6-P8-P7	101.8 (2)	P5-P6-Cr5	68.1 (1)
P1-P8-P7	108.1 (2)	P5-P6-Cr1	121.0 (2)
P4-P9-P1	104.9 (2)	P8-P6-Cr5	116.8 (2)
P4-P9-P2	101.9 (2)	P8-P6-Cr1	94.0 (2)
P1-P9-P2	79.8 (2)	Cr5-P6-Cr1	142.4 (2)
P7-P10-P2	106.8 (2)	P4-P7-P8	96.9 (2)
P7-P10-P3	100.5 (2)	P4-P7-P10	93.4 (2)
P2-P10-P3	79.8 (2)	P8-P7-P10	102.9 (2)
P8-P1-Cr1	91.9 (1)	P6-P8-P1	79.4 (2)
P9-P1-Cr2	98.2 (1)	P6-P8-P7	101.8 (2)
P9-P1-Cr1	115.3 (2)	P1-P8-P7	108.1 (2)
Cr2-P1-Cr1	132.9 (2)	P4-P9-P1	104.9 (2)
P10-P2-P9	102.7 (2)	P4-P9-P2	101.9 (2)
P10-P2-Cr2	115.4 (2)	P1-P9-P2	79.8 (2)
P10-P2-Cr3	91.9 (2)	P7-P10-P2	106.8 (2)
P9-P2-Cr2	97.9 (2)	P7-P10-P3	100.5 (2)
P9-P2-Cr3	112.0 (2)	P2-P10-P3	79.8 (2)
Cr2-P2-Cr3	134.0 (1)		

(c) Nearest Nonbonding Cr-P Distances (Å)

Cr1-P5	3.960 (4)	Cr3-P9	3.871 (4)
Cr1-P8	3.363 (4)	Cr3-P10	3.348 (4)
Cr1-P9	3.963 (4)	Cr4-P7	3.755 (4)
Cr2-P8	3.868 (4)	Cr4-P9	3.867 (4)
Cr2-P9	3.522 (4)	Cr4-P10	4.002 (4)
Cr2-P10	3.934 (4)	Cr5-P8	3.843 (4)

have been reported to contain only a simple monocyclic phosphane, e.g. cyclic  $\text{P}_6$  in  $\text{Ti}_2\text{P}_6\text{S}_1$ <sup>31</sup> and  $\text{Th}_2\text{P}_{11}$ .<sup>32</sup>

$\text{Cu}_4\text{SnP}_{10}$  is the only other known  $\text{M}_5\text{P}_{10}$  complex but, again, does not present an instance of coordination of

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organometallic metal groups to a polycyclic phosphane, and there is no similarity with  $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$ .  $\text{Cu}_4\text{-SnP}_{10}$  contains a quasi-tetrahedral  $[\text{SnCu}_3]$  cluster which interlinks four adamantane  $\text{P}_{10}^{6-}$  groups, thereby forming an extended structure containing six trimetallic six-membered rings as well as six bimetallic five-membered rings, all centered at Sn.<sup>33</sup> It is apparent there exists no similarity with the structure of 5, wherein five  $[(\eta^5\text{-C}_5\text{H}_5)\text{-Cr}(\text{CO})_2]$  fragments on the periphery of a  $\text{P}_{10}$  core form a discrete entity.

Considering a neutral core, the formal oxidation state of each Cr is +1. The molecule possesses a valence electron count of 125, 15 e per  $\text{CpCr}(\text{CO})_2$  fragment and 5 e per P atom. The magnetic moment and EPR spectrum are both in support of the presence of an unpaired electron, though a full interpretation of the complex EPR spectrum will require much more work than possible at this stage. It is apparent from the sharp resonances observed in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra that the effect of the odd electron on the Cp rings and the P atoms is negligible. This observation resembles those in biological molecules like

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HiPIP, where the presence of Fe(III) in its  $d^5$  high-spin state does not affect the proton resonance.<sup>34</sup> In this case, although the Cp ring signals appear in the normal region for diamagnetic Cp resonances, the variation in their line width from 3 to 12 Hz at ambient temperature may indicate a variation in proximity to the odd electron or different unpaired spin density environments.

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**Supplementary Material Available:** Tables of thermal parameters and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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