V. APPENDIX

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Novel Polycyclic Phosphane-to-Metal Coordination. Reaction of $[CpCr(CO)_3]_2$ with Elemental Phosphorus and Structure and Paramagnetism of the Odd-Electron Complex $[CpCr(CO)_2]_5P_{10}$

Lai Yoong Goh,*[,1a] Richard C. S. Wong,[1a] and Ekkehard Sinn*[,1b]

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 $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5 with 1.5 mol equiv of P_4 at 85 °C for 4 h resulted in the isolation of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)$ (2), $CpCr(CO)_2(\eta^3$-$P_3)$ (3), $Cp_2Cr_2(CO)_4$ (4), and $[CpCr(CO)_2]_5P_{10}$ (5) in 34, 34, 17, and 13% yields, respectively. The reaction of 4 with P_4 for 1.5 h, gave a similar mixture of 2, 3, and 5. The structure of the 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 μ_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 $P\bar{1}$ 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),[2] the coordination of polycyclophosphanes to metal atoms was unknown. This was soon followed by Dahl's synthesis of two Fe complexes containing the cagelike P_8 subunit of Hittorf's monoclinic phosphorus allotrope.[3] The complex (5) has been synthesized by taking advantage of the reactivity of the M–M bond in the dimer $[CpCr(CO)_3]_2$ (1).[4-6] Recent work on its reactions with the elemental chalcogens has led to the generation of some new dichromium complexes of S and Se.[7,8] The study of this reactivity with the non-metals was recently extended to elemental P_4[9] and has led to the isolation of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)$ (2) and $CpCr(CO)_2(\eta^3$-$P_3)$ (3) in substantially better yields than those reported for the analogous μ-η^2-P_2 and η^3-P_3 complexes obtained from the reaction of $Cp_2M_2(CO)_4$ (M = Cr, Mo, W and Cp = η^5-C_5H_5 or η^5-C_5Me_5) with elemental P_4.[10-12] We present here the results of further investigations which led to the isolation of additional products, $Cp_2Cr_2(CO)_4$ (4) and $[CpCr(CO)_2]_5P_{10}$ (5), together with an X-ray structural analysis of 5. Also described is a small-scale reaction of $Cp_2Cr_2(CO)_4$ (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 dribox equipped with a Model HE493 dri-train.

Reagents and Solvents. Yellow phosphorus was used as supplied by BDH Chemicals Ltd., without further purification. $[CpCr(CO)_3]_2$ was synthesized from $Cr(CO)_6$ (Aldrich Chemical Co.) as described by Manning.[13] 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. ^1H and ^{13}C NMR spectra were measured on a JEOL FX100 spectrometer, and chemical shifts referenced to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4Si$ in toluene-d_8. ^{31}P spectra were measured on the JEOL FX90Q FT, 36.23-MHz spectrometer and chemical shifts referenced to external H_3PO_4. IR spectra were measured in the range 4000–200 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.[14] Calibration and operation of this instrument were described elsewhere.[15,16] EPR spectra were run

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Table I. Product Composition from the Reaction of $[CpCr(CO)_3]_2$ (1) with Various Mole Equivalents of P_4[a]

Cr:P (mole)	reaction time (h)	products (% yields)				
		$Cp_2Cr_2(CO)_4P_2$ (2)	$CpCr(CO)_2P_3$ (3)	$Cp_2Cr_2(CO)_4$ (4)	$[CpCr(CO)_2]_5P_{10}$ (5)	others
1:1	3.5[b]	36	42	12	0	10 (unidentified δ 4.03)
	3.5[c,d]	19	14	16	6	
1:2	3.5[d,e]	53	40	0	0	
	1.25[b]	37	23	17	0	24 (unidentified δ 4.48 br)[i]
1:3	4[f,d]	34	34	17	13	
1:4	3.5[b,g]	37	45	0	18	
	10[b,g]	12	50	0	14	24 ($Cp_2Cr_2P_5$)[h]
	15[b,g]	2	33	0	22	43 ($Cp_2Cr_2P_5$)[h]

[a] In toluene, at 90 °C, unless otherwise stated. [b] Product yields by integration of Cp resonances in ^1H NMR spectrum of product mixture. [c] At 110 °C. [d] Product yields of isolated complexes. [e] From ref 9. [f] At 80–85 °C. [g] Aliquots of the same reaction mixture. [h] From ref 18. [i] 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 CH_2Cl_2 containing 0.5 M (n-Bu_4N)PF_6 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 $[CpCr(CO)_3]_2$ with P_4. (a) Isolation of $[CpCr(CO)_2]_5P_{10}$ (5) from 1:3 Cr:P Mole Ratio. A deep green suspension of $[CpCr(CO)_3]_2$ (200 mg, 0.50 mmol) and yellow 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 $CpCr(CO)_2P_3$ (3) (90 mg, 0.34 mmol, 34%) (^1H NMR (benzene-d_6): δ(Cp) 3.92[9]); (ii) a green fraction in n-hexane (20 mL) which yielded dark green solids of $Cp_2Cr_2(CO)_4$ (4) (30 mg, 0.087 mmol, 17%), characterized by its elemental analysis (Anal. Calcd for $[C_7H_5CrO_2]_2$: 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:[4] 205–206 °C]), its IR data (ν(CO) 1904 (vs), 1881 cm^{-1} (vs) (C_6D_6) [reported:[4] ν(CO) 1904, 1881 cm^{-1} (CS_2)]), and its ^1H NMR ((benzene-d_6): δ(Cp) 4.23) and MS data (m/z 346 ($Cp_2Cr_2(CO)_4$), 318 ($Cp_2Cr_2(CO)_3$), 290 ($Cp_2Cr_2(CO)_2$), 262 ($Cp_2Cr_2(CO)$), 234 (Cp_2Cr_2), 201 ($CpCr(CO)_3$), 182 (Cp_2Cr), 173 ($CpCr(CO)_2$), 145 ($CpCr(CO)$), and 117 ($CpCr$)); (iii) a magenta fraction in 1:1 n-hexane–toluene (20 mL) plus toluene (10 mL) which gave $Cp_2Cr_2(CO)_4P_2$ (2) (70 mg, 0.17 mmol, 34%) (^1H NMR (benzene-d_6): δ(Cp) 4.15[9]); (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 $[CpCr(CO)_2]_5P_{10}$ (5) (30 mg, 0.026 mmol, 13%). For 5: ^1H NMR (benzene-d_6) δ(Cp) 5.07, 4.90, 4.51, 4.43, 4.35; ^1H NMR (toluene-d_8) δ(Cp) 5.06, 4.90, 4.50 (relative intensity 1:1:3); ^{13}C NMR (benzene-d_6) δ(Cp) 89.72–88.82 (unresolved cluster of 4–5 peaks); IR ν(CO) 1925 (vs) 1855 cm^{-1} (s) (THF); FAB^+-MS m/z 1175.6 ($Cp_5Cr_5(CO)_{10}P_{10}$), 1119.6 ($Cp_5Cr_5(CO)_8P_{10}$), and 1063 ($Cp_5Cr_5(CO)_6P_{10}$); EI-MS m/z (parent ion not observed) unassigned peaks at 469 and 431, 389 ($Cp_2Cr_2P_5$), 358 ($Cp_2Cr_2P_4$), 327 ($Cp_2Cr_2P_3$), 296 ($Cp_2Cr_2P_2$), 266 ($CpCr(CO)_2P_3$), 262 ($CpCr_2P_3$), 238 ($CpCr(CO)P_3$), 213 (Cp_2CrP), 210 ($CpCrP_3$), 200 ($CpCr_2P$), 182 (Cp_2Cr), and 169 ($CpCr_2$). Anal. Calcd for $[C_7H_5CrO_2P_2]_5 \cdot C_6H_6$: 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 $[C_7H_5CrO_2P_2]_5 \cdot 0.5C_6H_6$: C, 37.56; H, 2.31. Found: C, 37.40, 37.04; H, 2.42, 2.49. The presence of C_6H_6 in the molecule was detected in its proton NMR spectrum in CD_2Cl_2.

(b) Isolation of $[CpCr(CO)_2]_5P_{10}$ (5) from 1:1 Cr:P Ratio. A similar reaction of $[CpCr(CO)_3]_2$ (500 mg, 1.24 mmol) with 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 $[CpCr(CO)_3]_2$ (50 mg, 0.124 mmol) and 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 C_6D_6 for a ^1H 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 $[CpCr(CO)_3]_2$ (1) to $[CpCr(CO)_2]_2$ (4). A solution of $[CpCr(CO)_3]_2$ (10 mg, 0.025 mmol) in toluene-d_8 (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 ^1H NMR spectrum, monitored at intervals, showed a slow conversion to 4 (δ 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 $[CpCr(CO)_2]_2$ (4) with P_4. To a solution of 4, prepared as described above from 1 (10 mg, 0.025 mmol) in toluene-d_8 (0.7 mL), was added 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 ^1H 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 δ 5.68, 1–2%, and $Cp_2Cr_2P_5$ δ 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 $Cp_2Cr_2P_5$ (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 $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_5P_{10}$ (5). This complex was obtained as an air-stable reddish brown crystalline solid, and diffraction-quality, chunky polyfaceted darkbrown 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 $P\bar{1}$ 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.[17,18]

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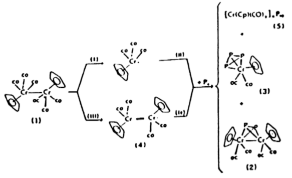
Scheme I



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 e/Å³.

Results and Discussion

Products and Reaction Pathways. An earlier report[9] described the isolation of $[CpCr(CO)_2]_2(\mu\text{-}\eta^2\text{-}P_2)$ (2) and $CpCr(CO)_2(\eta^3\text{-}P_3)$ (3) from the reaction of $[CpCr(CO)_3]_2$ with 1 mol equiv of 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, $[CpCr(CO)_2]_2$ (4), and $[CpCr(CO)_2]_5P_{10}$ (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 °C, or (b) *before* completion of reaction, e.g. 1.25 h at 90 °C or 4 h at 80–85 °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 indicted that 5 was thermally stable, as was 3, while 2 completely degraded to $Cp_2Cr_2P_5$ (^1H NMR (benzene-d_6): δ 18.8 ($\nu_{1/2}$ ca. 100 Hz).[19]

The detection and isolation of $[Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp]$ (4) necessitated control experiments involving the thermal decarbonylation of 1 as well as the cothermolysis of 4 with P_4 under similar reaction conditions, in order to diagnose the reaction pathways (Scheme I). Although Manning[4] had reported a facile thermal conversion (90%) of $[CpCr(CO)_3]_2$ 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 80–85 °C. Considering that the reaction of $[CpCr(CO)_3]_2$ with 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 (C_5Me_5) analogs of Cr, Mo, and W complexes,[10-12] can only constitute a subsidiary pathway. This indicates that our earlier proposed radical route,[9] shown as pathway ii, must be the predominant pathway, in agreement with the observed facile Cr—Cr bond dissociation 1[5,6,20-22] and accumulating evidence suggesting that reactions of 1 generally proceed via its 17-electron monomeric derivative.[5,6]

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 °C, though at 110 °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 °C, using a P:Cr mole equivalent of 3:1, also produces 5 (11%). These findings, together with earlier reports,[10-12] 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.[23,24]

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 cm⁻¹ (s). The FAB mass spectrum shows the parent ion m/z = 1175.6 ($Cp_5Cr_5(CO)_{10}P_{10}$) and two other P_{10}-containing ions, vis. m/z 1119.6 ($Cp_5Cr_5(CO)_8P_{10}$) and 1063 ($Cp_5Cr_5(CO)_6P_{10}$). In the EI mass spectrum, only mass fragments arising from $Cp_2Cr_2P_5$ and $CpCr(CO)_2P_3$[9] were observed. The proton NMR spectrum in benzene-d_6 shows five Cp resonances—two sharp peaks at δ 5.07 and 4.90 ($\nu_{1/2}$ 3 Hz) and three broader peaks at δ 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 °C, the two sharp peaks exhibit little change in their line widths or chemical shifts, which vary from δ 5.00 to 5.05 (i.e. $\Delta\delta$ = 0.05) and δ 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 °C are (i) δ = 4.38–4.54 (i.e. $\Delta\delta$ = 0.16) (ii) δ = 4.28–4.46 (i.e. $\Delta\delta$ = 0.18), and (iii) δ = 4.18–4.44 (i.e. $\Delta\delta$ = 0.26), respectively. Of these, the two higher-field resonances almost coalesce at 0 °C to give a broad peak centered at δ 4.34. At −50 and +90 °C, their line widths are all similar to those of the two sharp peaks at δ 5.00–5.05 and δ 4.84–4.87, respectively. The ^{13}C NMR spectrum shows an unresolved cluster of 4–5 peaks at δ 89.72–89.82. The ^{31}P NMR spectrum is illustrated in Figure 1. Owing to a lack of symmetry, 10 clusters of resonances are observed for the 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 $P_9{}^tBu_3$ and $P_{16}{}^{2-}$ had been found to possess P resonances between −180 and +150 ppm[23]

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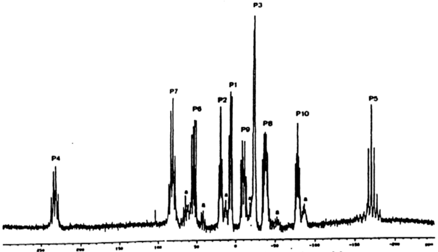

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $[CpCr(CO)_2]_5Pr_{10}$ (5). ^{a}From unknown impurities.

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

chemical shift (±0.2 ppm)	assgnt	multiplicity [J (±20 Hz)]	connectivities
+232.8	P4	ddd (430, 310,^{a} 370^a)	P5P7P9Cr4
+82.0	P7	ddd (310, 370,^{a} 340^a)	P4P8P10
+53.8	P6	dd (450, 260)	P5P8Cr1Cr5
+19.3	P2	dd (220,^{a} 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^a)	P4P6Cr5

^{a} Estimated from broad fine structure.

and between −180 and +60 ppm,[24] 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-memberd rings shifted to higher field.[25] 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[2] 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 1.5×10^{-3} T. The pattern is highly dependent on cyrstal orientation in the field, shows significant broadening at 20 K, and has all but disappeared at 50 K. The multiplicity of peaks 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 cm^{-1}). To analyze the spectrum further could require considerable more work, both experimentally and theoretically.

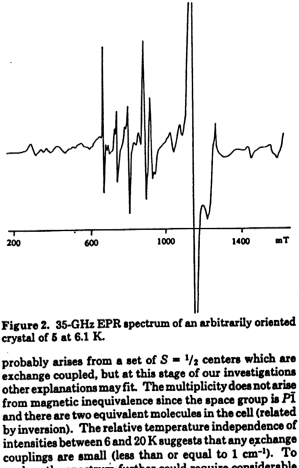

Figure 2. 35-GHz EPR spectrum of an arbitrarily oriented crystal of 5 at 6.1 K.

The magnetic moment of 1.75 μ_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[26] 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 δ 5.2–4.8. This reverted to the starting material within 1–2 h at ambient temperature [δ(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.[9] 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.[27] 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 $[CpCr(CO)_2]_2(\mu\text{-}\eta^2\text{-}P_2)$] and 2.427–2.494 Å for $[CpCr(CO)_2(\eta^3\text{-}P_3)]$.[9]

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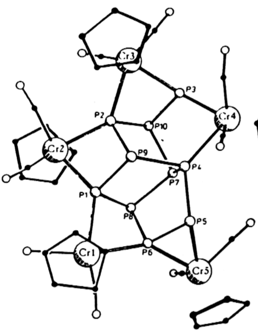

Figure 3. Structure of $[CpCr(CO)_2]_5P_{10}$ (5).

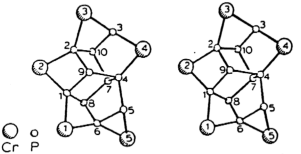

Figure 4. Stereoview of the Cr_5P_{10} unit of **5**. CO and Cp groups are removed for clarity.

Table IV. Selected Bond Lengths and Angles for $[CpCr(CO)_2]_5P_{10}$

(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)

Despite the syntheses of many polycyclophosphanes in the last two decades,[24,28] the bonding of such homocyclic annelated ring systems to organometallic fragments was previously unknown. The structure of **1** contains three homocyclic P_5 rings annelated like in the polyanion P_{16}^{2-} [28] 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 $CpCr(CO)_2$ fragments bridging across two P atoms. The closest examples are the iron complexes $Cp'_4Fe_4(CO)_6P_8$ and $Cp'_4Fe_6(CO)_{13}P_8$ ($Cp' = \eta^5\text{-}C_5H_4Me$) containing a regular-type α-P_8 core, wherein the coordination of the four bridgehead P atoms of the P_8 subunit of Hittorf's monoclinic phosphorus to $Cp'Fe(CO)_n$ fragments produces two four-membered FeP_3 rings in both complexes and an additional five-membered Fe_2P_3 ring in the second case.[3] The next nearest example involves the coordination of the P atoms of the cyclotriphosphane ring in the heptahetero–nortricyclene, $P_4[SiMe_2]_3$ to ML_n fragments,[29,30] and other known metal polyphosphides have been reported to contain only a simple monocyclic phosphane, e.g. cyclic P_6 in Ti_2P_6[31] and Th_2P_{11}.[32]

Cu_4SnP_{10} is the only other known M_5P_{10} complex but, (P10) 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 $[CpCr(CO)_2]_5P_{10}$. Cu_4SnP_{10} contains a quasi-tetrahedral $[SnCu_3]$ cluster which interlinks four adamantane 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.[33] It is apparent there exists no similarity with the structure of 5, wherein five $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]$ fragments on the periphery of a 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 $CpCr(CO)_2$ 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 ^1H and ^{31}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 HiPIP, where the presence of Fe(III) in its d^5 high-spin state does not affect the proton resonance.[34] 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 promixity 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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Synthesis and Thermolysis of Di- and Triarsenic Complexes of Chromium. Crystal Structure of $[CpCr(CO)_2]_2As_2$

Lai Yoong Goh* and Richard C. S. Wong

Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

Wai-Hing Yip and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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The cothermolysis of $[CpCr(CO)_3]_2$ ($Cp = \eta^5\text{-}C_5H_5$) with excess gray arsenic in refluxing toluene for 1–1.5 h resulted in the isolation of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}As_2)$ (**2**), $CpCr(CO)_2(\eta^3\text{-}As_3)$ (**3**), $Cp_2Cr_2(CO)_4(Cr{\equiv}Cr)$ (**4**), and $Cp_2Cr_2AsO_5$ (**6**) in 20.4, 14.2, 5.3, and 13.6% yields, respectively. The reaction when extended to 16 h gave **3**, $Cp_2Cr_2As_5$ (**5**), **6**, and $Cp_5Cr_5As_4O_8$ (**7**) in 5, 22, 39, and 8% yields, respectively. In refluxing xylene for 6 h, the reaction produced **3** (3%) and **7** (15%). **4** likewise reacted with excess elemental arsenic in refluxing toluene, yield **2** (18.5%), **3** (31.9%), and **6** (38.3%) after 1 h but only **2** (18.6%) and **6** (44.2%) after 5 h. Thermal degradation of **2** at 110 °C for 16 h yielded **6** (46.5%) and **7** (28%). **3** also degrades to **5**, but at a much slower rate. **2** crystallizes as dark purple needles. Crystal data: space group $C2/c$ (No. 15), $Z = 4$, $a = 15.551$ (3) Å, $b = 7.453$ (1) Å, $c = 13.446$ (2) Å.

Introduction

Since the first synthesis of the arsenic complexes $Co_2(CO)_6As_2$ and $Co(CO)_3As_3$ from the reaction of $Co_2(CO)_8$ with $AsCl_3$ and *cyclo*-$(MeAs)_5$, respectively,[1] and again later from the reaction of $Na[Co(CO)_4]$ with AsX_3 (X = Cl, Br, I),[2] there has been a gradual development in the role of these As_2 and As_3 units as ligands in complexes of other transition metals. Thus, diarsenic complexes have been derived from the reactions of the M—M-bonded $[CpM(CO)_3]_2$ dimers with *cyclo*-$(PhAs)_6$ (for M = Mo, $Cp = C_5H_5$),[3] with *cyclo*-$(MeAs)_5$ (for M = Mo, $Cp = MeC_5H_4$),[4] and with metallic As (for M = Mo, W, $Cp = C_5H_5$),[5] M≡M-bonded $[(C_5Me_5)Mo(CO)_2]_2$ with As_4S_4[6] and yellow As_4,[7] $CpW(CO)_3H$ with *cyclo*-$(PhAs)_6$,[3] $Na_2W_2(CO)_{10}$ or $W(CO)_5(THF)$ with $AsCl_3$,[8] $[(C_5Me_5)Mn(CO)_2(THF)]$ with AsH_3,[9] metal carbonyl fragment abstraction of $Cp(CO)_2MAs[Cr(CO)_5]_2$ (M = Mo, W), and reductive coupling of $Cp(CO)_2Mn_2AsCl$.[10] *cyclo*-As_3 complexes are less common. Only two other examples are known, viz. $(C_6Me_6)Mo(CO)_2As_3$[6] and the triple-decker $[(triphos)(Co)(As_3)Co(triphos)](PPh_4)_2$ complexes formed from the reaction

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of Co^{2+} with yellow As_4 in the presence of the triphos ($CH_3C(CH_2PPh_2)_3$) ligand.[11]

Having successfully developed in depth the reactivity of the highly reactive $[CpCr(CO)_3]_2$ dimer with elemental P_4,[12-14] we have extended the study to elemental gray arsenic and herein describe the results.

Experimental Section

General Procedures and Physical Measurements. Inert-atmosphere manipulation techniques and sources and preparation of reagents and solvents were as described previously.[12] Arsenic was obtained as the Fluka AG powder and was finely ground up before use. IR spectra were measured on a Perkin-Elmer 1330 instrument. ^1H NMR spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts are relative to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4Si$. ^{13}C NMR and mass spectra were measured at the Research School of Chemistry, Australian National University, which also carried out the elemental analyses, except for Cr, which we analyzed as CrO_4^{2-}.[15]

Cothermolysis Reactions with Elemental Arsenic. Reaction of $[CpCr(CO)_3]_2$ (1). A suspension of finely ground gray arsenic (1.23 g, 16.4 mmol) in a deep green solution of $[CpCr(CO)_3]_2$ (400 mg, 0.995 mmol) in toluene (ca. 20 mL) was stirred under gentle reflux for ca. 1 h. The reaction mixture had changed to purplish black. The mixture was concentrated to ca. 2 mL absorbed onto silica gel (ca. 1.5 g), and evacuated to dryness. It was then loaded onto a silica gel column (1.5 cm × 10 cm) prepared in *n*-hexane. Elution with *n*-hexane (5 mL) followed by a 9:1 *n*-hexane–toluene mixture (5 mL) gave a yellow fraction, which on concentration to dryness yielded fine yellow flakes of $CpCr(CO)_2As_3$ (**3**); 112 mg, 0.28 mmol, 14.2% yield). Anal. Calcd for $(C_5H_5)Cr(CO)_2As_3$: C, 21.13; H, 1.27; Cr, 13.06; As, 56.49. Found: C, 21.23; H, 1.28; Cr, 13.29; As, 56.49. IR: ν(CO) 1960 vs, 1905 vs cm^{-1} (toluene). ^1H NMR (C_6D_6): δ(Cp) 3.94. ^{13}C NMR (C_6D_6): δ(Cp) 83.04, δ(CO) 233.93. Further elution with a 1:1 *n*-hexane–toluene mixture (ca. 10 mL (gave a dirty green fraction (21 mg, dried residue), the ^1H NMR spectrum of which showed the presence of a 6:1 molar mixture of $[CpCr(CO)_2]_2(\mathit{Cr}{\equiv}\mathit{Cr})$ (**4**; δ 4.23, 5.3% yield) and **3** (δ 3.94, 0.4% yield), respectively. Continued elution with toluene (40 mL) gave a purple fraction, which when dried yielded fine dark purple crystalline solids of $[CpCr(CO)_2]_2As_2$ (**2**; 100 mg, 0.20 mmol, 20.4% yield). Anal. Calcd for $(C_5H_5)_2Cr_2(CO)_4As_2$: C, 33.90; H, 2.03; Cr, 20.97; As, 30.21. Found: C, 33.92; H, 1.92; Cr, 20.75; As, 30.36. IR: ν(CO) 1932 vs, 1875 vs cm^{-1} (toluene). ^1H NMR (C_6D_6): δ(Cp) 4.12. ^{13}C NMR: δ(Cp) 85.23, δ(CO) 239.31. MS: m/z 609 ($Cp_2Cr_2As_5$), 5.34 ($Cp_2Cr_2As_4$), 496 ($Cp_2Cr_2(CO)_4As_2$), 468 ($Cp_2Cr_2(CO)_3As_2$), 459 ($Cp_2Cr_2As_3$), 440 ($Cp_2Cr_2(CO)_2As_2$), 412 ($Cp_2Cr_2(CO)As$, 384 ($Cp_2Cr_2As_2$), 319 ($CpCr_2As_2$), 267 ($CpCrAs_2$), 192 (CpCrAs), 182 (Cp_2Cr), 117 (CpCr). The next fractions were a brown solution in ether (5 mL) and THF (5 mL) and a light green solution in CH_3CN (20 mL), each giving ca. 10 mg of mixtures of Cp-containing species that could not be separated for identification. The final fraction was a Prussian blue solution eluted with methanol (20 mL), which on concentration yielded a paramagnetic dark blue crystalline solid (53 mg; 13.6% yield based on its Cr content). Its elemental analysis indicated the empirical formula $(C_5H_5)_2Cr_2AsO_5$ (**6**). Attempts to grow a single crystal for a structural analysis have not proved successful so far.

A similar reaction for 16 h gave **3**, **5**, **6**, and **7** (described below) in yields of 5, 22, 39, and 8%, respectively.

Prolonged Reaction of $[CpCr(CO)_3]_2$ (1) at 140 °C. A suspension of finely ground gray arsenic (600 mg, 8.0 mmol) in a deep green solution of $[CpCr(CO)_3]_2$ (200 mg, 0.453 mmol) in xylene (10 mL) was refluxed with stirring for ca. 6 h. The resultant brown mixture was concentrated to ca. 1 mL and loaded onto a silica gel column (1 × 10 cm) prepared in *n*-hexane. Elution with *n*-hexane (5 mL) followed by a 1:1 *n*-hexane–toluene mixture (5 mL) gave a yellow fraction, from which $CpCr(CO)_2As_3$ (**3**) (12 mg, 0.03 mmol, 3% yield) was obtained. Elution with toluene (5 mL) followed by ether (5 mL) and finally a 1:1 ether–THF mixture (5 mL) gave a brown fraction, which on concentration to dryness yielded fine dark brown crystalline solids (50 mg). The ^1H NMR spectrum of these solids showed two broad peaks centered at δ 15.5 and 14.8. Chromatography of this brown product on a silica gel column (1 × 6 cm) prepared in *n*-hexane gave (i) a light brown fraction (11 mg residue, δ 14.8 and 11.3) eluted with 1:1 *n*-hexane–toluene (10 mL) (ii) a brown fraction eluted with toluene and ether (15 mL), which gave 29 mg of a dark solid (**7**; 15% yield based on Cr content, δ 14.8) (elemental analyses indicated the approximate molecular formula $(C_5H_5)_5Cr_5As_4O_8$, but this could not be structurally confirmed due to lack of a single diffraction-quality crystal), and (iii) a yellowish brown fraction (12-mg residue, δ 15.5 and 14.8) on further elution with a 1:1 ether–THF mixture (10 mL).

Reaction of $[CpCr(CO)_2]_2$ (4). A suspension of finely ground arsenic (215 mg, 2.87 mmol) in a deep green solution of $[CpCr(CO)_2]_2$ (60 mg, 0.173 mmol) in toluene (4 mL) was stirred under reflux for 1 h to give a dark purplish blue mixture.

A 2-mL aliquot of the supernatant solution was removed via a syringe, filtered through a 1-cm disk of Celite, and eluted with THF (ca. 3 mL). The filtrate/eluate was concentrated to dryness and the residue (33 mg) redissolved in toluene (ca. 1 mL) and loaded onto a column (1.5 × 2.5 cm) of silica gel prepared in *n*-hexane. Elution gave (1) a yellow fraction with *n*-hexane (15 mL), which yielded yellowish brown flakes of $CpCr(CO)_2As_3$ (**3**; 11 mg, 0.028 mmol, 31.9% yield), (ii) a purple fraction with 1:1 *n*-hexane–toluene (10 mL) followed by toluene (5 mL), from which was obtained fine purplish black crystalline solids of $[CpCr(CO)_2]_2As_2$ (**2**; 8 mg, 0.016 mmol, 18.5% yield), and finally (iii) a Prussian blue fraction with THF (20 mL), which yielded dark blue crystalline solids (**6**; 13 mg, 38.3% yield based on its Cr content).

The remaining aliquot in the flask was refluxed for a further 4 h, after which the resultant dark blue mixture was worked up via similar column chromatography. Elution gave (i) a purple fraction with 1:1 *n*-hexane–toluene (10 mL) followed by toluene (5 mL), which yielded **2** (8 mg, 0.02 mmol, 18.6% yield), (ii) a greenish brown fraction with 1:1 toluene–ether, which when dried gave an unidentified brown residue (2 mg), and (iii) a Prussian blue fraction with ether (5 mL) followed by THF (10 mL), which yielded fine dark blue crystalline solids of **6** (15 mg, 44.2% yield). A blue immovable band remained at the top of the column.

Thermolysis of $[CpCr(CO)_2]_2As_2$ (2). NMR Study. A purple solution of $[CpCr(CO)_2]_2As_2$ (**2**; 10 mg, 0.020 mmol) in toluene-d_8 (ca. 0.5 mL) in a 5-mm NMR tube vented via a syringe needle into a nitrogen line was maintained at ca. 110–115 °C, and its degradation was monitored by ^1H NMR spectroscopy at 0.5-h intervals. After 0.5 h, the spectrum showed three peaks corresponding to the presence of **2** (δ 4.12), **4** (δ 4.23), and $Cp_2Cr_2As_6$ (**5**; δ 23.5, $\nu_{1/2}$ 176 Hz) in the molar ratio of 3.5:2.8:1, respectively. After 5 h, **2** completely converted to a 1:1 molar mixture of **4** and **5**. After 18 h, **4** was no longer detected in the resultant brown solution but only **5** and two new broad peaks centered at δ 15.5 and 14.8 in the ratio of 2.5:1:1, with a substantial amount of a dark brown precipitate of $Cp_2Cr_2As_5$ (δ 23.5) at the bottom of the tube.

Product Isolation. A deep purple solution of $[CpCr(CO)_2]_2As_2$ (70 mg, 0.14 mmol) in toluene (10 mL) was stirred under nitrogen at reflux temperature for ca. 16 h. Filtration of the resultant brown solution gave ca. 25 mg (0.04 mmol, 29% yield) of dark brown amorphous solids of $Cp_2Cr_2As_5$ (δ 23.5). The filtrate, concentrated to ca. 1 mL, was loaded onto a silica gel column (1.5 × 7 cm) prepared in *n*-hexane. Elution with *n*-hexane (25 mL) followed by a 1:1 *n*-hexane–toluene mixture (10 mL) gave a golden yellow fraction, which on concentration yielded fine black crystalline solids of $Cp_2Cr_2As_5$ (15 mg, 0.025 mmol, 17.5% yield). Anal. Calcd for $(C_5H_5)_2Cr_2As_5$: C, 19.73; H, 1.66; Cr, 17.08. Found: C, 20.13; H, 1.67; Cr, 17.31. Further elution with a 1:1 toluene–ether mixture gave a brown fraction, which yielded 15 mg (28% yield) of a dark solid (**7**; δ14.8), described above. An immovable greenish

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Table I. Data Collection and Processing Parameters

mol formula	$[C_5H_5Cr(CO)_2]_2As_2$
mol wt	496.07
color and habit	dark-purple flat needles with (100) well developed
unit-cell params	$a = 15.551$ (3) Å $b = 7.453$ (1) Å $c = 13.446$ (2) Å $\beta = 96.21$ (2)° $V = 1549.4$ (4) Å^3 $Z = 4$ $F(000) = 960$
density (calcd)	2.127 g/cm^3
space group	$C2/c$ (No. 15)
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71073$ Å
std rflns	(222), (422)
intens variation	±1%
R_{int} (from merging of equiv rflns)	0.022
abs coeff	56.13 cm^{-1}
cryst size	0.40 × 0.32 × 0.04 mm^3
mean μr	0.025
transmissn factors	0.347–0.839
scan type and rate	ω–2θ; 2.93–14.65 deg min^{-1}
scan range	0.65° below Kα_1 to 0.65° above Kα_2
bkgd counting	stationary counts for 1/5 of scan time at each end of scan range
hkl collecn range	0–18, 0–8, −17 to +17; $2\theta_{max} = 50°$
no. of unique data measured	1201
no. of obsd data with $\lvert F_o\rvert \geq 6\sigma(\lvert F_o\rvert)$, n	893
no. of variables, p	100
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.034
weighting scheme	$w = [\sigma^2(F_o) + 0.0006\lvert F_o\rvert^2]^{-1}$
$R_G = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.040
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.141
resid extrema in final diff map	+0.34 to −0.42 e Å^{-3}

blue rim remained at the top of the column.

Thermolysis of $CpCr(CO)_2As_3$. A yellow solution of $CpCr(CO)_2As_3$ (3; 40 mg, 0.10 mmol) in toluene (4 mL) was thermolyzed with stirring under reflux. No color change was observed up to 7 h. After 21 h, the solution had turned slightly brownish with some dark precipitate. Filtration removed fine black crystalline solids of $Cp_2Cr_2As_6$ (5; 3 mg 0.005 mmol, 5% yield). The concentrated filtrate (ca. 1 mL) was loaded onto a column (1.5 × 3.5 cm) of silica gel prepared in *n*-hexane. Elution with *n*-hexane (15 mL) gave a yellow fraction, which yielded yellowish brown flakes on unreacted **3** (27 mg, 0.068 mmol, 68% yield). Further elution with toluene (10 mL) gave a golden yellow fraction, which yielded more fine black crystalline solids of **5** (8 mg, 0.013 mmol, 13% yield). A dark layer remained immovable at the top of the column.

Crystal Structure Analysis of 2. Single crystals of **2** were obtained as dark purple flat trapezoidal-shaped needles from toluene layered with *n*-hexane after 6 days at −30 °C.

Details of crystal parameters, data collection, and structure refinement are given in Table I. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile-fitting procedure of Diamond[16] and corrected for absorption with use of the ψ-scan data of eight selected reflections over the range $6 < 2\theta < 23°$.[17] Patterson superposition yielded the positions of all non-hydrogen atoms except those of the cyclopentadienyl group, which were derived from successive difference Fourier syntheses. All non-hydrogen atoms were subjected to anisotropic refinement, and the H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.12$ Å^2. No extinction correction was applied. Computations were performed with use of the SHELTXL-PLUS program package[18] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[19]

Table II. Atomic Coordinates (×10^5 for Cr and As; ×10^4 for Other Atoms) and Equivalent Isotropic Temperature Factors^a (×10^4 Å^2 for Cr and As; ×10^3 Å^2 for Other Atoms)

atom	x	y	z	U_{eq}
Cr(1)	41514 (6)	28153 (11)	18336 (6)	452 (3)
As(1)	54323 (4)	50593 (7)	18693 (4)	510 (2)
C(1)	4742 (5)	2347 (7)	758 (4)	64 (3)
O(1)	5074 (5)	1981 (8)	53 (3)	111 (3)
C(2)	3622 (5)	4711 (8)	1107 (5)	66 (2)
O(2)	3274 (4)	5839 (7)	636 (4)	91 (2)
C(3)	2810 (5)	2090 (11)	2034 (10)	115 (5)
C(4)	3322 (6)	1695 (9)	2927 (7)	92 (4)
C(5)	3917 (5)	365 (8)	2734 (5)	65 (2)
C(6)	3772 (6)	−35 (8)	1706 (6)	74 (3)
C(7)	3109 (6)	1019 (11)	1287 (8)	106 (4)

^{a} U_{eq} defined as one-third of the trace of the orthogonalized U tensor.

Results and Discussion

Products and Reaction Pathways. A deep green solution of $[CpCr(CO)_3]_2$ (**1**) underwent complete reaction under rigorous stirring with excess gray arsenic powder in refluxing toluene after 1–1.5 h. Column chromatography of the resultant purplish black solution led to the isolation of a μ-η^2-As_2 complex (**2**) as dark purple crystals (20.4% yield), a η^3-As_3 complex (**3**) as yellow crystalline flakes (14.2% yield), the known Cr≡Cr-bonded complex **4** (5.3% yield), and a Prussian blue complex of empirical formula $Cp_2Cr_2AsO_5$ (**6**); 13.6% yield), as shown in eq i, as well as

$$[CpCr(CO)_3]_2 \xrightarrow[1.5\ h/110\ °C]{As} \underset{\mathbf{2},\ 21.4\%}{[CpCr(CO)_2]_2As_2} + \underset{\mathbf{3},\ 14.2\%}{[CpCr(CO)_2(\eta^3\text{-}As_3)]} + \underset{\mathbf{4},\ 5.3\%}{[CpCr(CO)_2]_2(Cr\equiv Cr)} + \underset{\mathbf{6},\ 13.6\%}{[Cp_2Cr_2AsO_5]} + \text{others (very low yields)} \quad \text{(i)}$$

minor amounts of two as yet uncharacterizable Cp-containing species, showing bonds at δ 14.8 and 15.5 in the ^1H NMR spectrum. This facile reaction with elemental gray As under heterogeneous conditions is unusual. Only a few reactions of organotransition-metal complexes with elemental arsenic have been reported hitherto, and all but one of these invariably involved the use of the reactive yellow As_4 vapor dissolved in solution. Ziegler's reaction of the analogous Mo and W complexes with metallic As required more drastic conditions (24 h in refluxing xylene) to produce the respective μ-η^2-As_2 and $Cp_3M_3(CO)_6As$ complexes.[5] It is conceivable that the ease of reaction in this case derives from the high propensity of **1** to dissociate into its monomer radicals (eq ii).[20,21]

$$[CpCr(CO)_3]_2 \rightleftharpoons 2[CpCr(CO)_3^\bullet] \quad \text{(ii)}$$

Indeed, ample evidence has accumulated to indicate that all reactions of **1** occur via its monomeric form.[21] The subsequent radical attack of $CpCr(CO)_3^\bullet$ on elemental

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arsenic would generate the Cr–As complexes 2 and 3, as postulated for the analogous reaction with P_4.[12] However, as in all reactions of 1 under thermolytic conditions, the intermediatory role of $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ (4) arising from the decarbonylation of 1[12,14,22] always provides an alternative pathway. In this reaction, 4 was indeed isolated (5.3% yield) from the product mixture. Subsequently, it is herein demonstrated that the reaction of a suspension of 4 with a 16–17-fold molar excess of pulverized elemental arsenic reaches completion within 1 h in refluxing toluene, giving 2 (18.5), 3 (31.9%), and 6 (38.3%). An extended reaction period of 5 h gave 2 (18.6%) and 6 (44.2%).

This finding indicates the route via 4 could contribute substantially to the reaction. However, as in the reaction with P_4,[12,14] this contribution can only be subsidiary, judging from the short reaction time versus the longer time required for complete decarbonylation, which has been reported to exceed 2.5 h in refluxing toluene.[22] It is appropriate to note here that Scherer's reaction of the analogous $[Cp^*Mo(CO)_2]_2(Mo{\equiv}Mo)$ complex (Cp^* = η^5-C_5Me_5) with yellow As_4 in refluxing xylene (140 °C) gave, after 30 h, $[Cp^*Mo(CO)_2]_2(\mu$-η^2-$As_2)$ (1.2%), $Cp^*Cr(CO)_2(\eta^3$-$As_3)$ (15%), $[Cp^*Mo(CO)(\mu$-η^2-$As_2)]_2$ (1.7%), and *cis*-$[Cp^*_2Mo_2(\mu$-$O)_2O_2]$ (2%).[7]

Thermolytic Degradation of 2 and 3. Compared to the isolation of 2, 3, and 6 in 20.4%, 14.2%, and 13.6% yields, respectively, from 1 to 1.5 h reaction time in refluxing toluene, the reaction when extended to 16 h gave 3, 5, 6, and 7 in 5, 22, 39, and 8% yields, respectively. Prolonged cothermolysis of 1 with As in refluxing xylene (ca. 140 °C) for 6 h led to the isolation of 3 (3% yield) and a mixture of two Cp-containing species possessing δ(Cp) 14.8 and 15.5 in the ^1H NMR spectrum. These could be separated to give the former species in 15% yield (δ 14.8, approximate empirical formula $Cp_5Cr_6As_4O_8$ (7)). Indeed, an NMR study of the thermolytic degradation of 2 in toluene-d_8 at ca. 110 °C indicated a fairly rapid transformation to 4 and $Cp_2Cr_2As_5$ (5), which is spectrally detected at 30 min and is complete in 5 h to give a 1:1 millimolar mixture of 4 and 5. Further thermolysis to 18 h gave only 5 and the species possessing broad resonances at δ 14.8 and 15.5 mentioned above. A product isolation from the thermolysis of 2 after 16 h in refluxing toluene yielded 5 (46.5%) and 7 (δ 14.8, 28%).

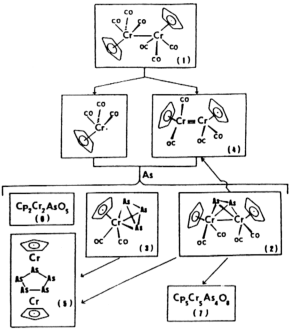
Likewise, 3 also thermally degrades to 5, though at a much slower rate (ca. 30% after 21 h in refluxing toluene). The thermolytic degradation of 2 and 3 to 5 is consistent with Scherer's isolation of only $Cp_2Cr_2As_5$ (5) in 37.7% yield from the reaction of 1 with yellow As_4 at 150 °C for 2.5-3 h.[23] Similarly, the forcing conditions employed (30 h, 150 °C) may be the cause of the low yield of the μ-η^2-As_2 complex (1.2%) from the reaction of the $[Cp^*Cr(CO)_2]_2$-$(Mo{\equiv}Mo)$ complex with yellow As_4.[7]

The observations described above are best presented schematically as in Scheme I. The findings are reminiscent of similar reaction and degradation pathways for the analogous P complexes[13,14] and indicate that, as in the case of the η^5-P_5 complex,[13] the formation of $Cp_2Cr_2As_5$ proceeds via thermal degradation of the μ-η^2-As_2 and η^3-As_3 complexes.

Properties and Spectral Characteristics. Deep purple crystals of the complex 2 are air-stable for extended periods at ambient temperature, whereas the yellow crystals of 3 are much less stable and definitely incapable of lasting several days in transit for an X-ray structural analysis. Both of these compounds dissolve readily in most organic solvents, giving purple and yellow solutions, respectively. A toluene solution of 2 exhibits ν(CO) at 1932 vs and 1875 vs cm^{-1}. The CO stretching frequencies of 3 in toluene at 1960 vs and 1905 vs cm^{-1} are strikingly similar to those of its analogous cyclo η^3-P_3 complexes (1975 vs and 1920 vs cm^{-1})[12] and point to a similarity in symmetry and structure. Both 2 and 3 are diamagnetic, and the Cp rings and CO ligands appear as singlets in both the ^1H and ^{13}C NMR spectra. These resonances of 2 (δ(Cp) 4.12 for ^1H and 85.23 for ^{13}C and δ(CO) 239.31) and of 3 (δ(Cp) 3.94 for ^1H and 83.04 for ^{13}C and δ(CO) 233.93) are very close to values obtained for their analogous μ-η^2-P_2 (δ(Cp) 4.15 and 86.4 and δ(CO) 238.60) and η^3-P_3 (δ(Cp) 3.92 and 84.91 and δ(CO) 233.74) complexes.[12] The Cp resonance of the complex 5 as reported before shows a paramagnetic downfield shift to δ 23.5 ($\nu_{1/2}$ 176 Hz).

The mass spectrum of 2 shows the parent ion and its fragmentation ions, as well as those of $Cp_2Cr_2As_5$ (5), which is consistent with its facile degradation to 5, which is consistent with its facile degradation to 5 observed under thermolytic conditions. Similar observations have been made for the analogous μ-η^2-P_2 complexes.[12]

Scheme I



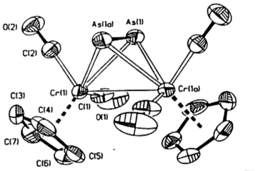


Figure 1. ORTEP drawing of the molecular structure of 2. The thermal ellipsoids are shown at the 35% probability level.

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Table III. Bond Lengths (Å) and Bond Angles (deg)

Cr(1)–Cr(1a)[a]	3.026 (1)	Cr(1)–As(1)	2.597 (1)
Cr(1)–As(1a)	2.452 (1)	As(1)–As(1a)	2.276 (1)
Cr(1)–C(1)	1.829 (7)	Cr(1)–C(2)	1.859 (6)
Cr(1)–X(1a)[b]	1.862 (6)	C(1)–O(1)	1.160 (9)
C(2)–O(2)	1.152 (8)	C(3)–C(4)	1.40 (1)
C(3)–C(7)	1.40 (2)	C(4)–C(5)	1.40 (1)
C(5)–C(6)	1.41 (1)	C(6)–C(7)	1.37 (1)
Cr(1a)–Cr(1)–As(1)	51.0 (1)	Cr(1a)–Cr(1)–As(1a)	55.4 (1)
As(1)–Cr(1)–As(1a)	53.5 (1)	Cr(1a)–Cr(1)–C(1)	89.3 (2)
As(1)–Cr(1)–C(1)	71.8 (2)	As(1a)–Cr(1)–C(1)	125.2 (2)
Cr(1a)–Cr(1)–C(2)	128.3 (2)	As(1)–Cr(1)–C(2)	79.4 (2)
As(1a)–Cr(1)–C(2)	85.6 (2)	C(1)–Cr(1)–C(2)	87.8 (3)
Cr(1a)–Cr(1)–X(1a)	114.0 (2)	AS(1)–Cr(1)–X(1a)	164.6 (2)
As(1a)–Cr(1)–X(1a)	117.3 (2)	C(1)–Cr(1)–X(1a)	115.1 (3)
C(2)–Cr(1)–X(1a)	113.7 (3)	Cr(1)–As(1)–Cr(1a)	73.6 (1)
Cr(1)–As(1)–As(1a)	60.0 (1)	Cr(1a)–As(1)–As(1a)	66.5 (1)
Cr(1)–C(1)–O(1)	175.7 (6)	CR(1)–C(2)–O(2)	177.4 (5)
C(4)–C(3)–C(7)	107.0 (7)	C(3)–C(4)–C(5)	108.5 (8)
C(4)–C(5)–C(6)	107.0 (6)	C(5)–C(6)–C(7)	108.5 (7)
C(3)–C(7)–C(6)	109.0 (8)		

[a] Symmetry transformation for a: $1 - x, y, {}^1/_2 - z$. [b] X(1a) is the center of the ring composed of carbon atoms C(3)–C(7).

Table IV. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[CpM(CO)_2]_2As_2$

	M = Cr[a]	M = Mo[3]	M = W[3]	$Co_2(CO)_5(PPh_3)As_2$[1]	$[(MeC_5H_4)Mo(CO)]_2(As_2)_2$[4]
M–M′	3.026 (1)	3.038 (2) 3.039 (2)	3.026 (2) 3.013 (2)	2.594[b]	2.950 (1)
As–As′	2.276 (1)	2.311 (3) 2.312 (3)	2.326 (5) 2.319 (5)	2.273 (3)	2.300 (2) 2.279 (2)
M–As	2.597 (1)	2.676 (2) 2.663 (2)	2.682 (3) 2.663 (3)	2.386 (av)	2.626 (1)
M–As′	2.452 (1)	2.569 (2) 2.567 (2)	2.573 (3) 2.571 (3)		
M–M′–As	55.4 (1)	53.0 (1) 53.0 (1)	53.2 (1) 53.4 (1)		
M′–M–As	51.0 (1)	56.3 (1) 56.0 (1)	56.5 (1) 56.3 (1)	57.1 (av)	
M–As–M′	73.6 (1)	70.8 (1) 71.0 (1)	70.3 (1) 70.3 (1)	65.8 (av)	
M–As–As′	66.5 (1) 60.0 (1)	61.5 (1) 61.6 (1)	61.3 (1) 61.7 (1)		
M′–As–As′	73.6 (1)	66.3 (1) 65.9 (1)	66.2 (1) 65.8 (1)	61.5 (av)	
As–M–As′	53.5 (1)	52.2 (1) 52.4 (1)	52.5 (1) 52.6 (1)	56.9 (av)	

[a] This work. [b] No esd was given in ref 3.

Molecular Structure of 2. A perspective view of the molecular structure with atom numbering is shown in Figure 1. The molecule is isostructural with the isomorphous Mo and W analogues,[3] having a μ-η^2-As_2 ligand bridging two Cr atoms, and also with the analogous μ-η^2-P_2 complex,[12] although the compounds crystallize in different space groups. The unit-cell dimensions of 2 are in fact consistent with those of the Mo and W analogues[3] with interchange of the *a* and *c* axes. Some selected bond lengths and bond angles are presented in Table III and compared in Table IX with those of the Mo and W analgues and two other structurally determined μ-η^2-As_2 complexes.

The As–As distance (2.276 Å) almost matches the shortest ever observed As–As bond (2.273 Å) in $Co_2(CO)_5(PPh_3)As_2$[1] and is significantly shorter than that in gaseous As_4 (2.44 Å)[24] and in the *cyclo*-polyarsines $[AsCH_3]_5$ (2.428 (8) Å)[25] and $[As(C_6H_5)]_6$ (2.456 (5) Å).[26] Dahl et al. had attributed this bond shortening to a partial charge transfer from the As_2 moiety to the metal fragment "electron sink", thereby decreasing electron-pair repulsion between the As atoms.[1] The Cr–Cr distance of 3.026 Å is close to that expected of a single bond.[20]

In the presence of a single metal–metal bond and on the assumption that the μ-η^2-As_2 ligand serves as a 4e donor, the noble-gas configuration at each Cr atom is achieved. The marginally shorter M–As and M–As′ distances in 2 could result from the smaller size of Cr when compared to those of Mo and W.

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Registry No. 1, 12194-12-6; 2, 132344-58-2; 3, 132344-59-3; 4, 54667-87-7; 5, 124273-44-5; As, 7440-38-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates for 2 (1 page); a listing of observed and calculated structure factor amplitudes for 2 (5 pages). Ordering information is given on any current masthead page.

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Acta Cryst. (1994). C50, 998–1000

A *cyclo*-Triarsenic Complex of Chromium

WEI CHEN,* R. C. S. WONG AND LAI-YOONG GOH

Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

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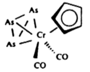
Abstract

The structure of dicarbonyl(η^5-cyclopentadienyl)(η^3-*cyclo*-triarsenido)chromium, [Cr(η^5-C_5H_5)$(CO)_2$(η^3-As_3)], has been determined. The *cyclo*-As_3 ligand possesses an average As—As distance of 2.338 Å and As—As—As angles of 59.71 (6), 60.32 (5) and 59.97 (6)°.

Comment

To date there have been only a few reports of tetrahedral metal–As_3 complexes (Dimaio & Rheingold, 1990). The first cyclotriarsenic complex reported was [Co$(CO)_3$(η^3-As_3)] (Foust, Campana, Sinclair & Dahl, 1969, 1979), which was obtained from the reaction of $Co_2(CO)_8$ with *cyclo*-$(PhAs)_6$ at 473 K in hexane under 100 atm (1 atm = 101.325 kPa) of CO. More than a decade later, [(C_5Me_5)Mo$(CO)_2$(η^3-As_3)] was isolated from the reaction of the triply bonded complex [(C_5Me_5)-Mo$(CO)_2$]$_2$ with As_4S_4 (Bernal, Brunner, Meier, Pfisterer, Wachter & Ziegler, 1984) and yellow As_4 (Scherer, Sitzmann & Wolmershäuser, 1986), respectively. The latter reaction with yellow As_4 was later extended to the analogous Cr≡Cr complex (Scherer, Wiedemann & Wolmershäuser, 1990) and to an Ru—Ru bonded complex (Scherer, Blath, Heckmann & Wolmershäuser, 1991). Recently, we have isolated [CpCr$(CO)_2$(η^3-As_3)] (Cp = η^5-C_5H_5), (I), from the reaction of the highly reactive [CpCr$(CO)_3$]$_2$ with elemental grey As (Goh, Wong, Yip & Mak, 1991). Its structure is described herein.



(I)

The molecular structure of the title compound is illustrated in Fig. 1. The molecule has similar geometry to those of the Mo (Bernal *et al.*, 1984) and the (C_5Me_5) analogues (Scherer *et al.*, 1990). The Cr atom is situated at the apex of a tetrahedron with an essentially equilateral basal As_3 triangle. The As—As bond lengths [2.331 (2)–2.346 (2) Å] fall between those of the single As—As bond (2.44 Å), as in As_4 (Maxwell, Hendricks & Mosley, 1935), and the As=As double bond (2.24 Å) (Cowley, Lasch, Norman & Pakulski, 1983; Cowley & Norman, 1986). There is good agreement with the values of As—As bond lengths in the (η^3-As_3) complexes known to date, as illustrated in Table 3. Foust *et al.* (1969) had attributed the shortening of the As—As bond length from that of the single-bond value in As_4 to a reduction in interarsenic repulsions by the introduction of the more electronegative organometallic fragment. The molecular structure is also similar to that of its (η^3-P_3) analogue (Goh, Chu, Wong & Hambley, 1989), with differences in *E*—*E* and *M*—*E* bond lengths (*E* = P, As) commensurate with the covalent radii of P and As.

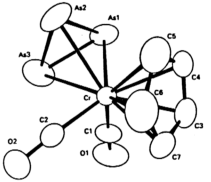


Fig. 1. Molecular structure of [Cr(η^5-Cp)$(CO)_2$(η^2-As_3)] with displacement ellipsoids drawn at the 50% probability level.

Experimental

The compound crystallized as golden brown plates from a saturated solution in toluene layered with hexane after 5-6 d at 245 K. The crystal used for data collection was coated in epoxy glue.

Crystal data

[Cr$(As_3)$$(C_5H_5)$$(CO)_2$]
M_r = 397.88
Monoclinic
$P2_1/a$
a = 7.537 (2) Å
b = 10.992 (1) Å
c = 12.670 (2) Å
β = 100.59 (1)°
V = 1031.7 (3) Å^3
Z = 4
D_x = 2.561 Mg m^{-3}

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–16°
μ = 10.58 mm^{-1}
T = 300 K
Plate
0.28 × 0.28 × 0.14 mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.580$, $T_{\max} = 0.999$
2063 measured reflections
1804 independent reflections
1189 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 400 reflections intensity variation: 0.026%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.043$
$S = 0.658$
1189 reflections
118 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0004F^2 + 1]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.90$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
As1	0.3365 (2)	0.1149 (1)	0.91273 (7)	4.72 (2)
As2	0.1542 (2)	−0.0587 (1)	0.90711 (8)	5.31 (2)
As3	0.0340 (2)	0.1217 (1)	0.82753 (9)	7.29 (3)
Cr	0.2623 (2)	0.0017 (1)	0.73393 (9)	2.58 (2)
O1	0.242 (1)	0.2379 (7)	0.6150 (6)	7.1 (2)
O2	−0.0982 (8)	−0.0558 (7)	0.6001 (5)	5.3 (2)
C1	0.248 (1)	0.1501 (9)	0.6640 (7)	4.2 (2)
C2	0.037 (1)	−0.0336 (8)	0.6543 (6)	3.4 (2)
C3	0.519 (1)	−0.013 (1)	0.6806 (8)	5.1 (2)
C4	0.541 (1)	−0.066 (1)	0.7798 (7)	5.6 (3)
C5	0.424 (1)	−0.164 (1)	0.7756 (9)	6.2 (2)
C6	0.329 (1)	−0.1728 (9)	0.6712 (9)	5.6 (2)
C7	0.387 (1)	−0.080 (1)	0.6109 (7)	5.1 (2)

Table 2. *Selected geometric parameters* (Å, °)

As1—As2	2.346 (2)	O2—C2	1.15 (1)
As1—As3	2.338 (2)	As1—Cr	2.555 (2)
As2—As3	2.331 (2)	As2—Cr	2.565 (1)
C3—C4	1.37 (1)	As3—Cr	2.619 (2)
Cr—C1	1.85 (1)	Cr—C2	1.85 (1)
C3—C7	1.41 (1)	Cr—C3	2.169 (9)
C4—C5	1.39 (2)	Cr—C4	2.207 (9)
Cr—C5	2.20 (1)	Cr—C6	2.17 (1)
C5—C6	1.39 (2)	Cr—C7	2.158 (9)
O1—C1	1.14 (1)	C6—C7	1.39 (2)
As2—As1—As3	59.71 (6)	As2—As1—Cr	62.95 (4)
As3—As1—Cr	64.54 (5)	As1—As2—As3	59.97 (6)
As1—As2—Cr	62.52 (4)	As3—Cr—C1	77.7 (3)
As3—As2—Cr	64.46 (5)	As3—Cr—C2	74.9 (3)
As1—As3—As2	60.32 (5)	As1—As3—Cr	61.76 (5)
As2—As3—Cr	62.10 (5)	As1—Cr—As2	54.53 (4)
As1—Cr—As3	53.70 (5)	As1—Cr—C1	88.8 (3)
C1—Cr—C2	87.5 (4)	As1—Cr—C2	128.0 (3)
As2—Cr—As3	53.44 (5)	As2—Cr—C1	129.7 (3)
As2—Cr—C2	90.5 (2)	Cr—C1—O1	175.5 (9)
C4—C3—C7	108 (1)	Cr—C2—O2	176.2 (7)
C3—C4—C5	109 (1)	C5—C6—C7	108 (1)
C4—C5—C6	108 (1)	C3—C7—C6	107 (1)

Table 3. *A comparison of* As—As *and* M—As *bond lengths* (Å) *in* (η^3-As$_3$) *complexes*

	As—As	*M*—As
$[\mathrm{Co(CO)_3(\eta^3\text{-}As_3)}]^a$	2.372 (5)	2.439 (5)
$[\mathrm{(C_5Me_5)Mo(CO)_2(\eta^3\text{-}As_3)}]^b$	2.372 (1)-2.377 (2)	2.639 (1)-2.706 (2)
$[\mathrm{(C_5Me_5)Cr(CO)_2(\eta^3\text{-}As_3)}]^c$	2.347 (2)-2.361 (2)	2.542 (1)-2.635 (2)
$[\mathrm{(C_5H_5)Cr(CO)_3(\eta^3\text{-}As_3)}]^d$	2.331 (2)-2.356 (2)	2.555 (2)-2.619 (2)
$[\{\mathrm{(C_5Me_4Et)Ru}\}_3\mathrm{Ru(\eta^3\text{-}As_3)\text{-}\mu_3\text{-}(\eta^3\text{-}As_3)(\mu_3\text{-}As_3)}]^e$	2.310 (7)-2.329 (1)*	2.521 (5)-2.536 (5)†

References: (*a*) Foust *et al.* (1969); (*b*) Bernal *et al.* (1984); (*c*) Scherer *et al.* (1990); (*d*) this work; (*e*) Scherer *et al.* (1991).

* In (η^3-As$_3$) ligand.
† For Ru to (η^3-As$_3$) ligand.

The structure was solved by direct methods with *MULTAN*80 (Main *et al.*, 1980); the H atoms were generated with C—H = 0.95 Å and were allowed to ride on their respective C atoms. Computer programs used for structure solution and refinement were from the *MolEN* (Fair, 1990) package and were run on a MicroVAX II minicomputer.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71704 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1050]

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Tetracarbonyliron Adducts of $Cp_2Cr_2(CO)_4(\mu-\eta^2-P_2)$. Syntheses and Crystal Structures of $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]_m$ ($m = 1$ and 2)

Lai Yoong Goh,[2] Richard C. S. Wong,[1] and Chen Wei[1]

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$Cp_2Cr_2(CO)_4(\mu-\eta^2-P_2)$, **1**, reacts with one molar equivalent of $Fe_2(CO)_9$ in THF to yield the mono- and di-iron complexes, $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]$, **2**, (16.5% yield) and $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]_2$, **3**, (16.9% yield), as dark magenta brown and dark greenish brown crystals, respectively. Both complexes were characterized by single-crystal X-ray diffraction analysis. Crystal data – **2**: space group = $P2_1/c$, $a = 17.024(1)$ Å, $b = 8.180(1)$ Å, $c = 30.891(2)$ Å, $\beta = 100.953(5)°$, $V = 4223.4(7)$ Å^3, $Z = 8$, 3743 observed reflections, $R_F = 0.033$; **3**: space group $P\bar{1}$, $a = 10.209(2)$ Å, $b = 10.212(2)$ Å, $c = 15.989(3)$ Å, $\alpha = 106.93(1)°$, $\beta = 91.87(1)°$, $\gamma = 119.50(1)°$, $V = 1356.5(4)$ Å^3, $Z = 2$, 3489 observed reflections, $R_F = 0.029$.

KEY WORDS: Cyclopentadienylchromium; diphosphido; tetracarbonyliron; structure.

INTRODUCTION

In its reactions with multinuclear transition metal complexes, the dinuclear iron carbonyl $Fe_2(CO)_9$ has been the source of the mononuclear fragments $Fe(CO)_n$ ($n = 2, 3$), resulting in cluster expansion [1]. In THF, it converts to the active solvento $Fe(CO)_4(THF)$ complex, leading often to interesting unexpected products [2]. In a continuing study of the coordinative ability of the $(\mu-\eta^2-P_2)$ ligand in $Cp_2Cr_2(CO)_4P_2$ [3], we have reacted it with $Fe_2(CO)_9$ in THF and herein report the results.

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[1] Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia.

[2] To whom all correspondence should be addressed.

EXPERIMENTAL

General Procedures

All reactions were carried out either by use of conventional Schlenk techniques under nitrogen or in an argon atmosphere in a Vacuum Atmospheres Dribox equipped with a Model HE 493 Dri-Train.

Solvents were distilled from sodium/benzophenone prior to use. $Cp_2Cr_2(CO)_4P_2$ **1** was synthesized from $Cp_2Cr_2(CO)_6$ [4]. $Fe_2(CO)_9$ was prepared from irradiation of $Fe(CO)_5$ in glacial acetic acid [5]. Silica gel (Merck Kieselgel 60, 35–70 mesh) was dried at 140°C before chromatographic use.

Table I. Data Collection and Processing Parameters

	Compound **2**	Compound **3**
Chemical formula	$[Cp_2Cr_2P_2(CO)_4][Fe(CO)_4]$	$[Cp_2Cr_2P_2(CO)_4][Fe(CO)_4]_2$
Molecular weight	576.06	743.95
Crystal system	Monoclinic	Triclinic
Space group	$P\,2_1/c$	$P\bar{1}$
a(Å)	17.024(1)	10.209(2)
b(Å)	8.180(1)	10.212(2)
c(Å)	30.891(2)	15.989(3)
α(°)	90.	106.93(1)
β(°)	100.953(5)	91.87(1)
γ(°)	90	119.50(1)
V(Å^3)	4223.4(7)	1356.5(4)
Z	8	2
D_c(Mgm^{-3})	1.812	1.82
μ(cm^{-1})	18.57	19.86
No. of unique reflections	6616	4765
θ max	24°	25°
No. observed reflections	3743	3489
$h_{min} \rightarrow h_{max}$	$0 \rightarrow 19$	$0 \rightarrow 12$
$k_{min} \rightarrow k_{max}$	$0 \rightarrow 9$	$-12 \rightarrow 10$
$l_{min} \rightarrow l_{max}$	$-35 \rightarrow 34$	$-18 \rightarrow 18$
No. of variables	639	401
R_F	0.033	0.029
$R_w(w = [\sigma^2(F) + 0.0004F^2 + 1])^{-1}$	0.038	0.034
S	0.389	0.491
$(\Delta/\sigma)_{max}$	0.11	0.01
$(\Delta\rho)$min/max(eÅ^{-3})	−0.107/0.292	−0.098/0.320

NMR spectra were measured on the following spectrometers: Jeol FX100 100 FT MHz, Jeol GSX270 270 FT MHz, and Varian VXR300 300 FT MHz instrument at the Research School of Chemistry, Australian National University. Chemical shifts were relative to residual solvent in C_6D_6 for ^1H and ^{13}C spectra and external H_3PO_4 for ^{31}P spectra. IR spectra were recorded on a JASCO IR REPORT-100 spectrometer. Mass spectra were run on Kratos AEI MS 3074. Elemental analyses were performed by the analytical unit of the Research School of Chemistry, Australian National University, except for Cr, which we determined as CrO_4^{2-} [6].

Reaction of 1 with $Fe_2(CO)_9$

A suspension of magenta **1** (150 mg, 0.37 mmol) and golden orange $Fe_2(CO)_9$ (134 mg, 0.37 mmol) in THF (10 ml) was stirred under an atmosphere of CO at 0°C. The mixture changed to a homogeneous brownish magenta solution after ca. 15 min. Celite (ca. 2 g) was then added and the mixture evacuated to dryness. The dry residue was loaded onto a silica gel column (1.5 × 13 cm) prepared in *n*-hexane. Elution gave 4 frac-

Table IIa. Positional and Equivalent Displacement Parameters for the Non-Hydrogen Atoms of **2**[a]

Atom	*x*	*y*	*z*	$B(\text{Å}^2)$
Fe1a	0.11424(5)	0.4424(1)	0.41739(3)	3.19(2)
Fe1b	0.60569(5)	0.3121(1)	0.91978(3)	3.21(2)
Cr1a	0.16305(6)	0.8164(1)	0.32429(3)	3.34(2)
Cr1b	0.66595(6)	0.6768(1)	0.82759(3)	3.25(2)
Cr2a	0.31259(5)	0.6605(1)	0.37490(3)	3.03(2)
Cr2b	0.81292(6)	0.5255(1)	0.88264(3)	3.17(2)
P1a	0.18292(9)	0.5854(2)	0.37468(5)	2.64(3)
P1b	0.68190(9)	0.4516(2)	0.88004(5)	2.84(3)
P2a	0.2085(1)	0.5492(2)	0.31309(5)	3.41(4)
P2b	0.7130(1)	0.4088(2)	0.81977(6)	3.65(4)
O1a	0.0217(3)	0.2515(9)	0.4689(2)	8.7(2)
O1b	0.4930(3)	0.1475(8)	0.9650(2)	7.8(2)
O2a	0.2588(3)	0.2619(8)	0.4560(2)	7.5(2)
O2b	0.7401(3)	0.1068(8)	0.9610(2)	6.7(1)
O3b	0.5885(4)	0.5912(8)	0.9766(2)	7.3(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

Table IIa. *Continued*

O3a	0.0957(4)	0.7273(8)	0.4717(2)	7.1(2)
O4b	0.5160(3)	0.1787(8)	0.8368(2)	6.8(2)
O4a	0.0129(3)	0.3138(8)	0.3374(2)	7.3(2)
O5a	0.1225(3)	0.9626(7)	0.4063(2)	6.2(1)
O5b	0.6176(3)	0.8234(6)	0.9072(2)	5.4(1)
O6a	−0.0031(3)	0.6794(8)	0.3033(2)	7.9(2)
O6b	0.5003(3)	0.5377(8)	0.8014(2)	7.4(2)
O7a	0.3900(3)	0.6629(8)	0.2951(2)	7.1(1)
O7b	0.8949(3)	0.5149(8)	0.8038(2)	7.0(1)
O8a	0.3524(3)	0.3038(6)	0.3783(2)	5.8(1)
O8b	0.8545(3)	0.1687(7)	0.8914(2)	6.8(2)
C1a	0.0583(4)	0.328(1)	0.4487(2)	5.2(2)
C1b	0.5370(4)	0.212(1)	0.9471(2)	5.0(2)
C2a	0.2029(4)	0.332(1)	0.4399(2)	4.5(2)
C2b	0.6889(4)	0.1892(9)	0.9445(2)	4.2(2)
C3b	0.5955(4)	0.489(1)	0.9532(2)	4.6(2)
C3a	0.1018(4)	0.618(1)	0.4493(2)	4.4(2)
C4b	0.5507(4)	0.236(1)	0.8687(2)	4.3(2)
C4a	0.0525(4)	0.367(1)	0.3683(2)	4.5(2)
C5a	0.1391(4)	0.9001(8)	0.3757(2)	4.0(2)
C5b	0.6373(4)	0.7621(8)	0.8772(2)	3.7(1)
C6a	0.0619(4)	0.7313(9)	0.3115(3)	4.8(2)
C6b	0.5638(5)	0.588(1)	0.8117(3)	5.0(2)
C7a	0.3581(4)	0.665(1)	0.3247(2)	4.9(2)
C7b	0.8611(4)	0.522(1)	0.8332(3)	4.9(2)
C8a	0.3370(4)	0.4393(9)	0.3771(2)	3.8(1)
C8b	0.8375(4)	0.3051(9)	0.8881(2)	4.5(2)
C11a	0.1362(6)	0.911(1)	0.2571(3)	7.1(2)
C11b	0.6398(6)	0.768(1)	0.7594(2)	6.1(2)
C12a	0.2175(5)	0.880(1)	0.2670(2)	6.1(2)
C12b	0.7215(5)	0.737(1)	0.7704(2)	5.9(2)
C13a	0.2515(5)	0.984(1)	0.3012(3)	5.6(2)
C13b	0.7546(5)	0.839(1)	0.8050(2)	5.4(2)
C14a	0.1905(5)	1.0755(9)	0.3133(3)	5.4(2)
C14b	0.6926(5)	0.9334(9)	0.8160(2)	5.2(2)
C15a	0.1176(6)	1.031(1)	0.2864(3)	6.4(2)
C15b	0.6221(5)	0.891(1)	0.7877(2)	5.6(2)
C21a	0.3091(4)	0.777(1)	0.4385(2)	4.5(2)
C21b	0.8066(4)	0.645(1)	0.9459(2)	4.7(2)
C22b	0.8237(4)	0.7664(9)	0.9177(2)	4.3(2)
C22a	0.3288(4)	0.9004(9)	0.4111(2)	4.4(2)
C23b	0.8959(4)	0.7263(9)	0.9058(3)	5.4(2)
C23a	0.4000(4)	0.854(1)	0.3990(3)	5.4(2)
C24b	0.9248(4)	0.581(1)	0.9260(3)	5.3(2)
C24a	0.4258(4)	0.703(1)	0.4199(3)	5.3(2)
C25b	0.8692(5)	0.533(1)	0.9521(3)	5.5(2)
C25a	0.3680(4)	0.655(1)	0.4446(2)	4.3(2)

Table IIb. Positional and Equivalent Displacement Parameters for the Non-Hydrogen Atoms of **3**[a]

Atom	*x*	*y*	*z*	B(Å^2)
Fe1	−0.21591(5)	0.31432(6)	0.71859(4)	3.35(1)
Fe2	0.09568(6)	0.06556(5)	0.78142(4)	3.36(1)
Cr1	0.22538(6)	0.41769(6)	0.65136(4)	2.65(1)
Cr2	0.26641(6)	0.57412(6)	0.84861(4)	2.64(1)
P1	0.03258(9)	0.39830(9)	0.74695(6)	2.55(2)
P2	0.15136(9)	0.28570(9)	0.75313(6)	2.55(2)
O1	−0.3269(4)	0.3113(5)	0.5476(3)	9.3(1)
O2	−0.4127(4)	0.2035(5)	0.8410(2)	7.9(1)
O3	−0.1522(4)	0.6360(4)	0.8214(3)	7.9(1)
O4	−0.2934(5)	−0.0186(4)	0.6370(3)	7.9(1)
O5	−0.1556(4)	0.0699(5)	0.8631(3)	8.0(1)
O6	0.2637(5)	0.1256(4)	0.9532(3)	9.2(1)
O7	−0.1365(5)	−0.2538(4)	0.6596(3)	7.6(1)
O8	0.3151(4)	0.0267(4)	0.6788(3)	7.9(1)
O9	0.1052(4)	0.6165(3)	0.6149(2)	6.00(9)
O10	−0.0535(4)	0.1315(4)	0.5182(2)	6.1(1)
O11	0.1133(4)	0.4284(4)	0.9823(2)	6.2(1)
O12	0.5011(3)	0.4907(4)	0.8852(3)	5.93(9)
C1	−0.2811(5)	0.3165(6)	0.6150(3)	5.5(1)
C2	−0.3331(5)	0.2494(5)	0.7944(3)	4.8(1)
C3	−0.1750(4)	0.5129(5)	0.7795(3)	4.9(1)
C4	−0.2618(5)	0.1115(6)	0.6679(3)	5.1(1)
C5	−0.0568(5)	0.0704(5)	0.8329(3)	5.0(1)
C6	0.2013(6)	0.1039(5)	0.8864(4)	5.5(1)
C7	−0.0452(5)	−0.1271(5)	0.7059(3)	4.7(1)
C8	0.2336(5)	0.0453(5)	0.7199(4)	4.9(1)
C9	0.1499(4)	0.5411(4)	0.6308(3)	3.8(1)
C10	0.0514(4)	0.2395(5)	0.5701(3)	3.8(1)
C11p	0.3456(5)	0.4343(6)	0.5421(3)	5.4(1)
C11	0.1696(5)	0.4811(4)	0.9303(3)	3.9(1)
C12p	0.3452(4)	0.3181(6)	0.5716(3)	5.5(1)
C12	0.4104(4)	0.5192(4)	0.8694(3)	3.8(1)
C13p	0.4294(4)	0.3923(5)	0.6596(3)	4.6(1)
C14p	0.4835(4)	0.5567(5)	0.6832(3)	4.3(1)
C15p	0.4302(4)	0.5817(5)	0.6118(3)	4.5(1)
C21p	0.3748(5)	0.8006(4)	0.8170(3)	4.3(1)
C22p	0.4696(5)	0.8195(5)	0.8887(3)	4.6(1)
C23p	0.3921(6)	0.8026(5)	0.9583(3)	5.3(1)
C24p	0.2470(5)	0.7736(5)	0.9282(3)	5.4(1)
C25p	0.2344(5)	0.7705(4)	0.8408(3)	4.5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

tions:—(1) a yellowish green fraction in *n*-hexane (20 ml) which yielded a minute amount of a dark green solid (ca. 5 mg) of an unidentifiable compound, possessing a cluster of cp resonances at δ 4.48, 4.41, 4.31, and 4.209 in its proton NMR spectrum. (2) a magenta solution in 3:7 toluene–hexane (30 ml) which gave unreacted **1** (21 mg, 0.051 mmol, 13.9%). (3) a brownish magenta fraction in 7:3 toluene–hexane, which yielded fine dark crystalline solids of $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]$, **2** (145 mg, 0.25 mmol, 68.5%

Table IIIa. Bonding Parameters of **2**[a]

Cr1a	Cr2a	3.006(2)			
Cr1b	Cr2b	3.011(2)			
Fe1a	P1a	2.250(2)	Cr1b	C6b	1.862(9)
Fe1a	C1a	1.752(8)	Cr1b	C11b	2.199(8)
Fe1a	C2a	1.784(9)	Cr1b	C12b	2.212(9)
Fe1a	C3a	1.781(9)	Cr1b	C13b	2.219(9)
Fe1a	C4a	1.782(8)	Cr1b	C14b	2.191(9)
Fe1b	P1b	2.258(2)	Cr1b	C15b	2.188(8)
Fe1b	C1b	1.767(8)	Cr2a	P1a	2.290(2)
Fe1b	C2b	1.787(8)	Cr2a	P2a	2.515(2)
Fe1b	C3b	1.807(9)	Cr2a	C7a	1.862(8)
Fe1b	C4b	1.786(8)	Cr2a	C8a	1.855(8)
Cr1a	P1a	2.430(2)	Cr2a	C21a	2.193(8)
Cr1a	P2a	2.366(2)	Cr2a	C22a	2.250(8)
Cr1a	C5a	1.844(8)	Cr2a	C23a	2.201(8)
Cr1a	C6a	1.829(9)	Cr2a	C24a	2.180(8)
Cr1a	C11a	2.180(9)	Cr2a	C25a	2.180(8)
Cr1a	C12a	2.211(9)	Cr2b	P1b	2.298(2)
Cr1a	C13a	2.248(9)	Cr2b	P2b	2.514(2)
Cr1a	C14a	2.211(8)	Cr2b	C7b	1.866(9)
Cr1a	C15a	2.170(9)	Cr2b	C8b	1.851(9)
Cr1b	P1b	2.434(2)	Cr2b	C21b	2.206(8)
Cr1b	P2b	2.362(2)	Cr2b	C22b	2.238(8)
Cr1b	C5b	1.833(8)	Cr2b	C23b	2.195(8)
Cr2b	C24b	2.159(8)	Cr2b	C25b	2.178(9)
P1a	P2a	2.052(2)	P1b	P2b	2.060(2)
O1a	C1a	1.148(9)	O1b	C1b	1.142(8)
O2a	C2a	1.140(9)	O2b	C2b	1.142(8)
O3b	C3b	1.124(9)	O3a	C3a	1.143(9)
O4b	C4b	1.149(8)	O4a	C4a	1.146(9)
O5a	C5a	1.156(8)	O5b	C5b	1.157(8)
O6a	C6a	1.167(9)	O6b	C6b	1.143(9)
O7a	C7a	1.148(8)	O7b	C7b	1.165(9)
O8a	C8a	1.138(9)	O8b	C8b	1.153(9)
$\langle C–C \rangle_{cp}$		1.40(1)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IIIa. *Continued*

P1a	Fe1a	C1a	177.7(3)	P1a	Cr1a	C6a	81.6(3)
P1a	Fe1a	C2a	89.8(2)	P1a	Fe1a	C3a	92.0(2)
P1a	Fe1a	C4a	88.2(2)	C1a	Fe1a	C2a	91.3(4)
C1a	Fe1a	C3a	89.5(4)	C1a	Fe1a	C4a	89.5(4)
P2a	Cr1a	C5a	126.9(2)	C2a	Fe1a	C3a	112.0(4)
P2a	Cr1a	C6a	86.4(3)	C2a	Fe1a	C4a	118.4(4)
C3a	Fe1a	C4a	129.5(4)	P1b	Fe1b	C1b	173.9(3)
P1b	Fe1b	C2b	91.5(2)	P1b	Fe1b	C3b	91.9(2)
P1b	Fe1b	C4b	87.3(2)	C5a	Cr1a	C6a	88.5(4)
C1b	Fe1b	C2b	94.5(4)	C1b	Fe1b	C3b	87.4(4)
C1b	Fe1b	C4b	88.7(3)	C2b	Fe1b	C3b	111.1(4)
C2b	Fe1b	C4b	115.0(4)	C3b	Fe1b	C4b	133.9(4)
P1a	Cr1a	P2a	50.65(6)	P1a	Cr1a	C5a	76.3(2)
C5b	Cr1b	C6b	89.1(3)	P1b	Cr1b	P2b	50.85(6)
P1b	Cr1b	C5b	75.2(2)	P1b	Cr1b	C6b	82.0(3)
P2b	Cr1b	C5b	126.0(2)	P2b	Cr1b	C6b	86.0(3)
P1a	Cr2a	P2a	50.30(6)	P1a	Cr2a	C7a	123.8(3)
P1a	Cr2a	C8a	87.0(2)	P2a	Cr2a	C7a	73.6(3)
P2a	Cr2a	C8a	78.2(2)	P1b	Cr2b	P2b	50.45(6)
C7a	Cr2a	C8a	85.5(3)	P1b	Cr2b	C7b	122.8(3)
P1b	Cr2b	C8b	87.0(2)	P2b	Cr2b	C7b	72.5(3)
P2b	Cr2b	C8b	79.0(3)	Fe1a	P1a	Cr1a	139.04(8)
C7b	Cr2b	C8b	86.1(4)	Fe1a	P1a	Cr2a	138.22(8)
Fe1a	P1a	P2a	134.0(1)	Cr1a	P1a	Cr2a	79.05(6)
Cr1a	P1a	P2a	63.04(8)	Cr2a	P1a	P2a	70.55(8)
Fe1b	P1b	Cr1b	137.86(9)	Fe1b	P1b	Cr2b	140.20(9)
Fe1b	P1b	P2b	132.7(1)	Cr1b	P1b	Cr2b	78.98(7)
Cr1b	P1b	P2b	62.76(8)	Cr2b	P1b	P2b	70.23(8)
Cr1a	P2a	Cr2a	75.97(7)	Fe1a	C2a	O2a	177.2(7)
Cr1a	P2a	P1a	66.30(8)	Cr2a	P2a	P1a	59.15(7)
Cr1b	P2b	Cr2b	76.20(7)	Fe1b	C2b	O2b	177.3(7)
Cr1b	P2b	P1b	66.39(8)	Fe1b	C3b	O3b	174.6(7)
Cr2b	P2b	P1b	59.32(7)	Fe1a	C1a	O1a	179.2(9)
Fe1a	C3a	O3a	176.5(7)	Fe1b	C4b	O4b	176.1(8)
Fe1a	C4a	O4a	177.5(8)	Fe1b	C1b	O1b	179.5(7)
Cr1a	C5a	O5a	175.1(7)	Cr1b	C5b	O5b	176.2(7)
Cr1a	C6a	O6a	178.9(7)	Cr1b	C6b	O6b	178.1(8)
Cr2a	C7a	O7a	176.1(8)	Cr2b	C7b	O7b	176.0(8)
Cr2a	C8a	O8a	180.(1)	Cr2b	C8b	O8b	178.5(7)
⟨C–C–C⟩			108.0(9)				

yield), and (4) a dirty green fraction in toluene (20 ml), which yielded dark crystalline solids of $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]_2$, **3** (45 mg, 0.06 mmol, 16.5% yield). The brown rim at the top of the column was eluted with ether (10 ml) and THF (25 ml). However, the residue showed a featureless proton NMR spectrum.

Table IIIb. Bonding Parameters of 3[a]

Cr1	Cr2	2.999(1)			
Fe1	P1	2.221(1)	Cr2	C12	1.864(5)
Fe1	C1	1.774(6)	Cr2	C21p	2.241(4)
Fe1	C2	1.767(5)	Cr2	C22p	2.202(5)
Fe1	C3	1.796(6)	Cr2	C23p	2.165(5)
Fe1	C4	1.791(6)	Cr2	C24p	2.171(5)
Fe2	P2	2.221(1)	Cr2	C25p	2.221(5)
Fe2	C5	1.800(6)	P1	P2	2.058(1)
Fe2	C6	1.794(6)	O1	C1	1.138(6)
Fe2	C7	1.764(5)	O2	C2	1.142(6)
Fe2	C8	1.803(6)	O3	C3	1.137(6)
Cr1	P1	2.498(1)	O4	C4	1.139(6)
Cr1	P2	2.322(1)	O5	C5	1.131(6)
Cr1	C9	1.863(5)	O6	C6	1.129(6)
Cr1	C10	1.855(5)	O7	C7	1.141(6)
Cr1	C11p	2.167(5)	O8	C8	1.131(6)
Cr1	C12p	2.174(5)	O9	C9	1.148(5)
Cr1	C13p	2.227(5)	O10	C10	1.139(5)
Cr1	C14p	2.242(4)	O11	C11	1.140(5)
Cr1	C15p	2.198(4)	O12	C12	1.140(5)
Cr2	P1	2.322(1)	Cr2	P2	2.498(1)
Cr2	C11	1.862(5)	C13p	C14p	1.403(7)
C14p	C15p	1.390(8)	C21p	C22p	1.380(7)
C11p	C12p	1.397(9)	C21p	C25p	1.401(7)
C22p	C23p	1.388(8)	C11p	C15p	1.391(8)
C12p	C13p	1.396(8)	C23p	C24p	1.398(9)
C24p	C25p	1.388(8)			

P1	Fe1	C1	114.1(2)	P1	Cr1	C10	81.6(1)
P1	Fe1	C2	121.0(2)	P1	Fe1	C3	91.0(2)
P1	Fe1	C4	89.9(2)	C1	Fe1	C2	124.9(2)
C1	Fe1	C3	93.1(3)	C1	Fe1	C4	91.8(3)
P2	Cr1	C9	123.5(1)	C2	Fe1	C3	87.1(2)
P2	Cr1	C10	86.8(1)	C2	Fe1	C4	87.5(2)
C3	Fe1	C4	174.2(2)	P2	Fe2	C5	90.1(2)
P2	Fe2	C6	114.2(2)	P2	Fe2	C7	121.0(2)
P2	Fe2	C8	91.0(2)	C9	Cr1	C10	87.3(2)
C5	Fe2	C6	91.2(3)	C5	Fe2	C7	87.5(2)
C5	Fe2	C8	174.2(2)	C6	Fe2	C7	124.8(2)
C6	Fe2	C8	93.6(3)	C7	Fe2	C8	87.1(2)
P1	Cr1	P2	50.39(3)	P1	Cr1	C9	73.2(1)
C11	Cr2	C12	87.0(2)	P1	Cr2	P2	50.38(3)
P1	Cr2	C11	86.9(1)	P1	Cr2	C12	123.5(1)
P2	Cr2	C11	81.6(1)	P2	Cr2	C12	73.2(1)
Fe1	C2	O2	177.8(6)	Fe1	P1	Cr1	133.88(5)
Fe1	P1	Cr2	145.88(5)	Fe1	P1	P2	133.75(6)
Fe1	C3	O3	176.5(5)	Cr1	P1	Cr2	76.87(3)
Cr1	P1	P2	60.37(4)	Cr2	P1	P2	69.26(4)
Fe2	P2	Cr1	145.83(5)	Fe2	P2	Cr2	133.95(5)
Fe2	P2	P1	133.77(6)	Fe1	C4	O4	178.4(5)
Cr1	P2	Cr2	76.86(3)	Cr1	P2	P1	69.24(4)
Cr2	P2	P1	60.36(4)	Fe1	C1	O1	177.2(7)
Fe2	C5	O5	178.0(6)	Fe2	C6	O6	177.9(6)
Fe2	C7	O7	177.5(5)	Cr2	C11	O11	177.9(4)
Fe2	C8	O8	177.1(5)	Cr1	C9	O9	177.3(4)
Cr1	C10	O10	177.9(4)	Cr2	C12	O12	177.3(4)
⟨C–C–C⟩			108.0(6)				

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[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

For **2**: NMR (C_6D_6), ^1H δ(cp) 4.14; ^{13}C δ(cp) 87.32, δ(CO) unresolved cluster of peaks with main resonances at 215.48 and 214.87; $^{31}P\{^1H\}$ δ28.20 (*d*, *J* 499Hz) and 151.25 (*d*, *J* 499Hz). IR (nujol, cm^{-1}) ν(CO) at 2045vs, 1978vs, 1935s sh, 1920s sh. Anal. Calc.: C, 37.76; H, 1.67; Cr, 17.20; P, 10.26; Fe, 9.26%. Found: C, 37.93; H, 1.62; Cr, 18.06; P, 10.78 and Fe 9.21%. Electron impact mass spectrum: *m/z* 576[$Cp_2Cr_2(CO)_4P_2Fe(CO)_4$], 492[$Cp_2Cr_2(CO)_4P_2Fe(CO)$], 464[$Cp_2Cr_2(CO)_4P_2Fe$], 436[$Cp_2Cr_2(CO)_3P_2Fe$], 408[$Cp_2Cr_2(CO)_4P_2$], 380[$Cp_2Cr_2(CO)_3P_2$], 352[$Cp_2Cr_2(CO)_2P_2$], 324[$Cp_2Cr_2(CO)P_2$], 296[$Cp_2Cr_2P_2$], 182[$Cp_2Cr$] and 169[CpCr].

For **3**: ^1H NMR(C_6D_6): δ(cp) 4.16; $^{31}P\{^1H\}$ $\delta-33.22$ (*d*, *J* 505Hz) and 51.09 (*d*, *J* 505Hz). IR(nujol, cm^{-1}): ν(CO) at 2060s, 2050s, 1970vs, br, 1949s sh, 1927s. Anal. Calc.: C, 35.55; H, 1.35; Cr, 13.98, P, 8.33 and Fe, 15.02%. Found: C, 35.54; H, 1.43; Cr, 14.45; P, 7.44 and Fe, 14.31%.

Crystal Structure Analysis

Quality crystals of **2** and **3** were obtained from saturated solutions in toluene layered with hexane. Dark magenta brown rectangular plates of **2** and dark greenish brown trapezoidal shaped plates of **3** were collected after 3 and 7 days, respectively, at −28°C.

Accurate cell dimensions and space group data were obtained from 25 strong reflections in the $14° < \theta < 16°$ shell of the crystals with cell sizes of less than 0.3 mm in each dimension. Three standard reflections were used to monitor the intensity. The data were collected using the $\omega - 2\theta$ method with MoK_α radiation.

The parameters used in data collection and processing are summarized in Table I. Lorentz-polarization, linear decay and absorption corrections were applied. An empirical Fourier Method (DIFABS) [7] was used for compound **2** while another empirical psi-scan method [8] was used for compound **3**.

Compound **2** was solved by the direct method SIMPEL [9] while compound **3** was solved by the direct method SIR [10]. All non-H atoms were refined anisotropically. The H atoms obtained from successive difference Fourier syntheses were refined isotropically. Analytic expressions of neutral atom scattering factors were employed [11] and anomalous dispersion corrections were incorporated [12].

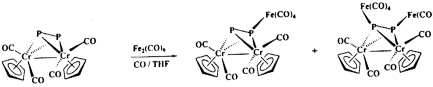
Data were collected on a four circle CAD4 diffractometer at 26°C and computer programs for structural solution and refinement are from the MolEN package [13] and performed on a MicroVAX-II mini-computer.

Positional parameters for the non-hydrogen atoms and their equivalent displacement parameters are presented in Tables IIa and b.

The structure factor tables and anisotropic displacement parameters for the two structures are deposited as supplementary materials.

RESULTS AND DISCUSSION

A heterogeneous 1:1 molar mixture of **1** and $Fe_2(CO)_9$ underwent a facile reaction in THF under an atmosphere of CO at 0°C within ca. 15 min to give a homogeneous brownish magenta solution from which were isolated dark magenta-brown crystals of the mono-iron complex **2** (68.5% yield) and greenish–brown crystal of the di-iron complex **3** (16.5% yield), as represented in Scheme 1, together with some unreacted substrate **1** and a trace of an unidentifiable compound. The reaction is reminiscent of the coordination of the lone electron pairs of the P_2 unit of **1** to $M(CO)_5(THF)$ ($M = Cr$ [3], Mo and W [14]), and earlier similar reactions of $Cp_2Mo_2(CO)_4P_2$ studied by Scherer [15] and of $Co_2(CO)_5LP_2$ ($L = CO$, PBu_3, PPh_3) studied by Markó [16]. Therein was described the first instance of the coordination of the $(\mu-\eta^2-P_2)$ unit to a $Fe(CO)_4$ fragment. Similar coordination to two $Fe(CO)_3$ units was achieved in $[Fe(CO)_3]_2(\mu-CO)(P_2)[Cr(CO)_5]_2$, obtained from the reaction of $Fe_2(CO)_9$ with $(CO)_5CrPBr_3$ [17]. However, $(\mu-\eta^2-P_2)$ complexes containing $Fe(CO)_m$ ($m = 3$ or 4) fragments are still of rare occurrence, though the coordination of the phosphene unit ($-P=P-$) to $Fe(CO)_4$ is rather common [1].



1 **2** **3**

Scheme 1

Crystal Structures

The perspective drawings of **2** and **3** are illustrated in Figs 1 and 2, respectively. Their respective bonding parameters are given in Tables IIIa and b.

As shown in Table IV, the lengths of the Cr–Cr bonds in **2** and **3** are very close to that of their parent **1** (3.011(1) Å), for which a single bond has been indicated [4, 18]. On the basis of this and on the assumption that

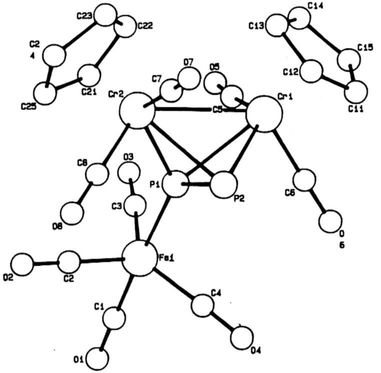


Fig. 1. Perspective drawing of 2.

Table IV. Some Selected Bond Lengths (Å) and Bond Angles (°) in 2 and 3, and Its Parent Compound 1

	2	3	1
Cr–Cr	3.006(2), 3.011(2)	2.999(1)	3.011(1)
P1–P2	2.052(2), 2.060(2)	2.058(1)	2.060(1)
Fe–P	2.250(2), 2.258(2)	2.221(1), 2.221(1)	—
Cr–P	2.290(2)–2.515(2)	2.322(1)–2.498(1)	2.34(1), 2.474(1)
Cr–P–P	59.15(7)–70.55(8)	60.36(4)–69.26(4)	61.4(1), 68.1(1)
P–Cr–P	50.30(6)–50.85(6)	50.38(3), 50.39(3)	50.5(1), 50.6(1)
Cr–P–Fe	137.86(9) – 140.20(9)	133.88(5) – 145.88(5)	–
Cr–P–Cr	75.97(7) – 79.05(6)	76.86(3), 76.87(3)	77.2(1), 77.5(1)
Fe–P–P	132.7(1), 134.0(1)	133.77(6), 133.75(6)	–
Cr–Cr–P	48.41(5) – 54.27(5)	48.92(3) – 54.22(3)	49.4(1), 53.2(1)
Cr–P–P–Cr	−92.48, −92.66	−86.33	−87.18
Cr–P–P–Fe	131.28, −141.20	124.00 – −149.67	–

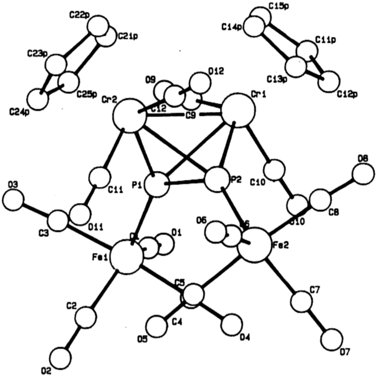


Fig. 2. Perspective drawing of 3.

the $\mu-\eta^2-P_2$ ligand serves as a 4e donor, each Cr atom achieves the noble gas configuration. The P–P length in **1** (2.060 Å) is only very slightly shortened by the coordination of one $Fe(CO)_4$ fragment (2.056 Å, av.) or two (2.058 Å). These values lie within the range [2.019(9)–2.154(4) Å] [19] of P–P distances in $\mu-\eta^2-P_2$ complexes to date. Their significant difference from the single bond P–P distance (2.21 Å) in P_4 vapor [20], probably arises from the ability of the organometallic fragment(s) to act as an "electron sink," thus causing a reduction in electron-pair repulsions between the P atoms and resulting in P–P bond shortening, as was rationalized by Dahl [21] and Sacconi [22, 23] for similar As and P complexes, respectively.

The bonding parameters of the $Cr_2P_2Fe_m$ $(m = 1, 2)$ core compare favorably with the parent $Cp_2Cr_2(CO)_4P_2$, especially in the more symmetrical compound **3** as illustrated in Table IV. A larger range observed for

⟨Cr–P–Fe⟩ in **3** is consistent with steric hindrance due to the two $Fe(CO)_4$ groups which are deviated from each other by a torsional angle (Fe1–P1–P2–Fe2) of −25.56°. The significant difference between the structure of the two compounds lies in the geometry about the Fe atoms. In compound **2**, the P is coordinated axially while in compound **3** both P atoms are coordinated equatorially to the trigonal bipyramidal Fe atoms. This change of geometry about Fe will ensure that the two equatorial planes do not intersect with each other, in order to alleviate steric hindrance.

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Unprecedented Cage-Opening of P_4S_3 Initiated by an Organometallic Radical: Synthesis and Structure of $[Cp_4Cr_4(CO)_9(P_4S_3)]$**

By *Lai Yoong Goh*,* *Wei Chen*, and *Richard C. S. Wong*

We recently found that $[CpCr(CO)_3]$ radical-induced cleavage of P_4 and As_4 tetrahedra leads to the abstraction of $(\mu\text{-}\eta^2\text{-}E_2)$ and $(\eta^3\text{-}E_3)$ moieties (E = P, As) as ligands,[1, 2] and more interestingly, to a unique aggregation of P atoms to yield the novel $[\{CpCr(CO)_2\}_5P_{10}]$ complex.[3] We have now extended our study to cage compounds like P_4S_3, and we describe here the reaction of $[\{CpCr(CO)_3\}_2]$ with P_4S_3 which proceeds without fragmentation to form the title compound **1**, a new polyphosphido-sulfido complex.

$[Cp_4Cr_4(CO)_9(P_4S_3)]$ **1**

Previous examples of P_4X_3 (X = S, Se) as a ligand in transition metal complexes involve the coordination of intact P_4X_3 cages (through the apical P atom) with the metal center (Fig. 1), for example in *cis*-$[(P_4S_3)_2M(CO)_4]$ (M = Cr, Mo, W) and *cis*-$[(P_4S_3)_3M'(CO)_3]$ (M' = Cr, Mo),[4] $[Mo(CO)_5(P_4S_3)]$,[5] and $[(np_3)Ni(P_4X_3)]$ (X = S, Se; $np_3 = [N(CH_2CH_2PPh_2)_3]$).[6] In contrast, in the presence of the chelating ligand triphos (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane), the reaction of P_4X_3 (X = S, Se) with $Co(BF_4)_2 \cdot 6H_2O$[7, 8] and $[RhCl(cod)]_2$ (cod = cycloocta-1,5-diene),[9] resulted in fragmentation of the P_4X_3 cage, yielding the complexes $[(triphos)Co(P_2X)]BF_4$ and $[(triphos)Rh(P_3X_3)]$, respectively. In its reaction with $[\{Cp^*Mo(CO)_2\}_2]$ (*Mo≡Mo*) ($Cp^* = \eta^5\text{-}C_5Me_5$), the P_4S_3 cage likewise underwent fragmentation giving a mixture of $[Cp^*Mo(CO)_2P_3]$, $[Cp^*_2Mo_2(CO)_4P_2]$, $[Cp^*_2Mo_2P_2S_3]$, and $[Cp^*_2Mo_2P_4S]$.[10] In reactions with the square-planar d^8 metal complexes $[IrCl(CO)(PPh_3)_2]$ (Vaska's complex) or $[Pt(C_2H_4)(PPh_3)_2]$, cleavage of a single P–P bond in the basal P_3 triangle of the cage led to the $[\mu\text{-}P_4S_3]$-bridged binuclear $[\{Ir(\mu\text{-}P_4S_3)(PPh_3)Cl(CO)\}_2]$[11] and trinuclear $[\{Pt(\mu\text{-}P_4S_3)(PPh_3)\}_3]$[12] complexes, respectively.

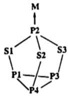

Fig. 1. Coordination of P_4S_3 to a metal complex fragment M.

$[\{CpCr(CO)_3\}_2]$ and P_4S_3 (1 molequiv) in toluene were allowed to react at ambient temperature for 13 days. The compounds **1** (66%), $[\{CpCr(CO)_2\}_2S]$ (8%; yields based on $[\{CpCr(Co)_3\}_2]$ employed), unreacted P_4S_3 (38%), and an as-yet-unidentified yellow crystalline complex were isolated from the reaction mixture following column chromatography on silica gel. Complex **1** was eluted with toluene/hexane (7:3) as a reddish brown fraction, and isolated as a dark brown crystalline solid which has been characterized by analytical and spectroscopic methods.[13] Dark brown platelets of **1** suitable for a single-crystal X-ray structural analysis[14] (Fig. 2) were obtained from a THF/Et_2O solution, after three weeks at −30 °C.

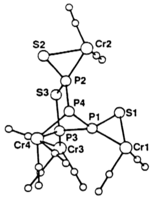

Fig. 2. Molecular structure of **1** (Cp rings omitted for clarity).

From Figure 2, it is apparent that the cleavage of the P2–S1, P4–S2, and P3–P4 bonds, with concomitant bond formation between P2 and P4, gives a five-membered P_4S ring with two external sulfur atoms as substituents, namely S1 at P1 and S2 at P2, as found in the structure of **1**. Together with Cr4, this five-membered ring forms a bicyclo[2.1.1] system, possessing common vertices at P3 and P4. In fact, the P_4S ring bridges four $[CpCr(CO)_n]$ (*n* = 2 or 3) fragments through its four P atoms; the S atom of the five-membered ring is not coordinated to a metal center. With the exception of Cr3, the other three Cr atoms are coordinated to two atoms of the P_4S_3 ligand. It should be noted that P3 is the only P atom that bridges two Cr atoms (Cr3 and Cr4), the Cr4–P3 distance is 0.084 Å shorter than that between P3 and Cr3. Cr1 and Cr2 have similar ligand environments, both possessing a pseudo η^2-PS ligand. An earlier example of η^2-PS coordination was established for the $Cr(CO)_5$ adduct of $[Cp^*_2Mo_2P_4S]$.[10] Each of the five-coordinate Cr atoms assumes a four-legged piano-stool geometry.

The P–P bond lengths (mean 2.201 Å) in **1** are significantly shorter than those in the P_4S_3 cage (mean 2.235 Å),[15] and are very close to the value for the single bond (2.21 Å) in P_4 vapor.[16] The P–S distances (mean 2.0067 Å) in **1** are also shorter than in the intact cage (mean 2.090 Å).[15] The Cr–P distances (mean 2.282 Å) in the CrPS rings for Cr1 and Cr2 are significantly shorter than the other three Cr–P bonds (mean 2.440 Å), which fall within the range 2.341–2.494 Å observed for other CpCr complexes with phosphorus ligands.[1, 3] The Cr–S distances (2.486 and 2.517 Å) in **1** are longer than those observed in $Cr(\mu\text{-}\eta^2\text{-}S_2)$ and $Cr(\mu\text{-}\eta^1,\eta^2\text{-}S_2)$ complexes (range 2.348–2.466 Å).[17]

In summary, this is the first example of multiple bond cleavage without fragmentation of the P_4S_3 cage by a transition metal complex. Slight cage rearrangement has been observed before in the insertion of a $Cr(CO)_5$ fragment into the isostructural nortricyclic homopolyatomic Zintl ion As_7^{3-}.[18] A very recent example of this reaction type is the insertion of three Ni(CO) fragments into Sb_7^{3-}.[19] The extensive cage opening cum structural rearrangement of the neutral P_4S_3 cage described here is unprecedented and may be attributed to the unusual reactivity of the radical-like

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[*] Prof. Dr. L. Y. Goh, Dr. W. Chen, R. C. S. Wong (M.Sc)
Department of Chemistry, University of Malaya
59100 Kuala Lumpur (Malaysia)
Telefax: Int. code + (3)75-66343

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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.[13]

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[13] Satisfactory elemental analysis. ^1H NMR (300 MHz, C_6D_6, 25 °C, residual C_6H_6): The spectrum indicates a 2:1 molar mixture of isomers A and B. Isomer A: $\delta(Cp) = 4.58(s), 4.61(s), 4.76(s), 4.77(d, J = 1.5$ Hz) and isomer B: $\delta(Cp) = 4.61(s), 4.70(s), 4.79(d, J = 1.5$ Hz) and 4.86(s). A variable-temperature ^1H NMR study in $C_6D_5CD_3$ shows that isomer A is the predominant species below −30 °C ($\delta(Cp) = 4.39, 4.53, 4.63$ and 4.71), and that rapid exchange of the four Cp rings at 90 °C gives rise to a singlet at $\delta = 4.77$. ^{13}C NMR (67.80 MHz, C_6D_6): $\delta(Cp) = 91.71, 92.07, 92.72, 93.15$. IR(toluene): $\tilde{\nu}[cm^{-1}] = 2028vs, 1983vs, 1969vs, 1950vs, 1942vs, 1899s, 1882sh s, 1874vs$ (CO).

[14] Crystal data for 1: $M_r = 1012.66$, triclinic, space group $P\bar{1}$, $a = 12.074(1)$, $b = 12.880(3)$, $c = 14.451(5)$ Å, $\alpha = 73.05(2)$, $\beta = 73.21(1)$, $\gamma = 78.67(1)^\circ$, $V = 2042.5(9)$ Å^3, $Z = 2$, $\varrho = 1.646$ Mg m^{-3}, $F(000) = 1020$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 13.65$ cm^{-1}, $T = 27$ °C, crystal dimensions: 0.1 × 0.2 × 0.15 mm. Enraf-Nonius CAD4 diffractometer, ω-2θ scan mode. Of 6208 reflections measured, 3221 ($I > 3\sigma(I)$) were used in refinement. The crystal used for unit cell determination and data collection was coated with epoxy glue to prevent decomposition in air. Twenty-five strong reflections were used for accurate determination of the unit cell parameters. The measured intensities were processed for Lorentz-polarization effects and decay; and corrected for absorption [20]. The structure was solved by direct methods (MULTAN). All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically with a distance of 0.95 Å to the carbon atoms and were allowed to "ride" with $B = 1.3$. A THF solvent molecule was found at a general position in the unit cell and was disordered. The positional parameters for the THF ring were fixed, while their displacement parameters were refined as carbon atoms. Residual peaks in the final difference map account mainly for peaks around the THF molecule. Computations were performed by using the MolEN [21] package on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated [22]. Final $R = 0.048$, ($R_w = 0.057$). Further details of the crystal structure investigation are available from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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