Chemistry of [{Cr(cp)(CO)$_3$}$_2$], (cp = η^5-C$_5$H$_5$). Reaction with Elemental P$_4$. A High Yield Synthesis and Crystal Structures of [{Cr(cp)(CO)$_2$}$_2$(μ-η^2-P$_2$)] and [Cr(cp)(CO)$_2$(η^3-P$_3$)]†

Lai Yoong Goh,* C. K. Chu, and Richard C. S. Wong
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia
Trevor W. Hambley*
Department of Inorganic Chemistry, The University of Sydney, New South Wales 2006, Australia

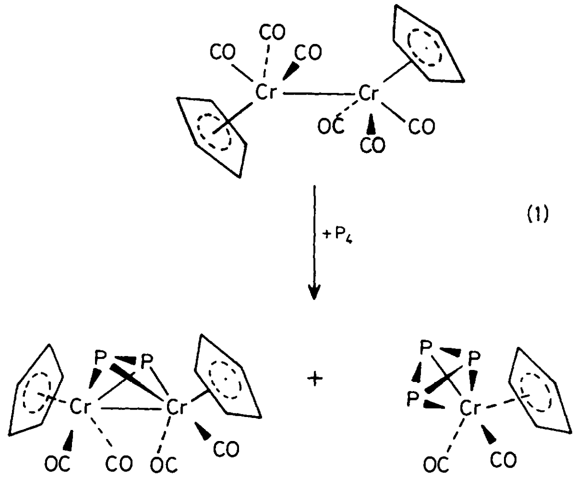
---

The reaction of [{Cr(cp)(CO)$_3$}$_2$] (cp = η^5-C$_5$H$_5$) with 1 molar equivalent of P$_4$ in toluene at 90 °C gave [{Cr(cp)(CO)$_2$}$_2$(P$_2$)] and [Cr(cp)(CO)$_2$(P$_3$)] (**2**) in 53 and 40% yields, respectively. A radical mechanism has been postulated. Single-crystal *X*-ray diffraction studies show that (**1**) contains a μ-η^2-P$_2$ group bridging two metal–metal bonded Cr atoms and (**2**) contains a tricyclo-η^3-P$_3$ ligand. Crystal data: (**1**) monoclinic, space group $P2_1/n$, a = 7.934(2), b = 17.189(3), c = 11.327(2), β = 97.69(2)°, and Z = 4; (**2**) monoclinic, space group $P2_1/c$, a = 11.398(3), b = 14.383(1), c = 13.323(4), β = 115.32(2)°, and Z = 8. The synthetic method, structures, and spectral features of these complexes are compared with those of analogous complexes of other transition metals, particularly Mo.

The study of metal–metal bonded complexes has for the last two decades been an area of active research.[1,2] Our own contribution has included an investigation of the reaction of the Cr–Cr bonded [{Cr(cp)(CO)$_3$}$_2$] dimer (cp = η^5-C$_5$H$_5$) with elemental chalcogens.[3,4] In view of the current interest in transition-metal complexes containing bare P atoms or units,[5–7] and with cognizance of the extremely high reactivity of [{Cr(cp)(CO)$_3$}$_2$],[3,4,8,9] we have treated this species with elemental yellow P$_4$ and herein report our findings.

Results and Discussion

Synthetic Pathways.—A thermolytic reaction at 90 °C for 3.5 h of a 1:4 molar mixture of [{Cr(cp)(CO)$_3$}$_2$] and elemental yellow phosphorus in toluene led to the isolation of a μ-η^2-P$_2$ complex (**1**) and a η^3-P$_3$ complex (**2**) as dark magenta crystals (53% yield) and dark brown crystals (40% yield), respectively. The reaction as represented in equation (1) suggests a dual pathway, involving effectively the insertion of a P$_2$ fragment into the Cr–Cr single bond of [{Cr(cp)(CO)$_3$}$_2$] and the cleavage of the same bond by a P$_3$ fragment, with the concomitant expulsion of CO ligands. Formally, in so much as this involves the reaction of a metal–metal bond, this reaction finds some semblance in the reaction of [Co$_2$(CO)$_8$] with P$_4$ [equation (2)][10] and in Scherer's recently reported reactions of triply bonded M≡M complexes with P$_4$, as depicted in equation (3),[11,12] though these reactions required more forcing conditions. To date, there has not been any speculation or study on the mechanism of these reactions. However, on the basis of the documented high proclivity of [{Cr(cp)(CO)$_3$}$_2$] to dissociate into radicals in solution[13,14] [equation (4)] and the substitution lability of such 17e species,[15–17] it is conceivable that the initial step involves a radical attack of [Cr(cp)(CO)$_3$]$^\bullet$ and/or Cr(cp)(CO)$_2$]$^\bullet$ on the P$_4$ tetrahedron resulting in P–P bond cleavages, with simultaneous or subsequent abstraction of P$_3$, P$_2$, and P$_1$ fragments to form [Cr(cp)(CO)$_2$(P$_3$)] (**2**) and substituted radicals [Cr(cp)(CO)$_2$(P$_2$)]$^\bullet$ and [Cr(cp)(CO)$_2$P]$^\bullet$. Subsequent coupling processes as represented in equation (5) will then generate the μ-η^2-P$_2$ complex (**1**). Such a radical mechanism has been proposed for the facile formation of [{Cr(cp)(CO)$_2$}$_2$E] (E = S or Se) and [{Cr(cp)(CO)$_2$}$_2$Se$_2$] from [{Cr(cp)(CO)$_3$}$_2$] and E$_8$.[4b] There is ample support for the coupling of such metal- centred substituted radicals from the work of Brown[15,16b] and Wrighton and co-workers.[17] Thus, it is probable that the much higher yields of (**1**) and (**2**) as compared with those of the analogous complexes from the reactions of [Co$_2$(CO)$_8$][10] and [(OC)$_2$LM≡ML(CO)$_2$] [M = Cr, L = C$_5$Me$_5$;[12a] M = Mo, L = C$_5$H$_5$[11a] or C$_5$Me$_5$;[11b] M = W, L = C$_5$Me$_5$[12b]] is a direct consequence of the radical mechanism. Though not postulated before for organometallic reactions, there has been a lot of evidence for such radical-initiated reactions of elemental white P$_4$ with organic substrates.[18] Thus a radical attack on the P$_4$ tetrahedron was demonstrated in the involvement of (*a*) P$_4$(CCl$_3$)$^\bullet$ in the photochemical or γ-ray induced conversion of P$_4$ in CCl$_4$ into red P, PCl$_3$, and PCl$_2$(CCl$_3$),[19] (*b*) P$_4$(OBu^t)$^\bullet$ in the t-butoxy



(1)

(**1**) 53%   (**2**) 40%

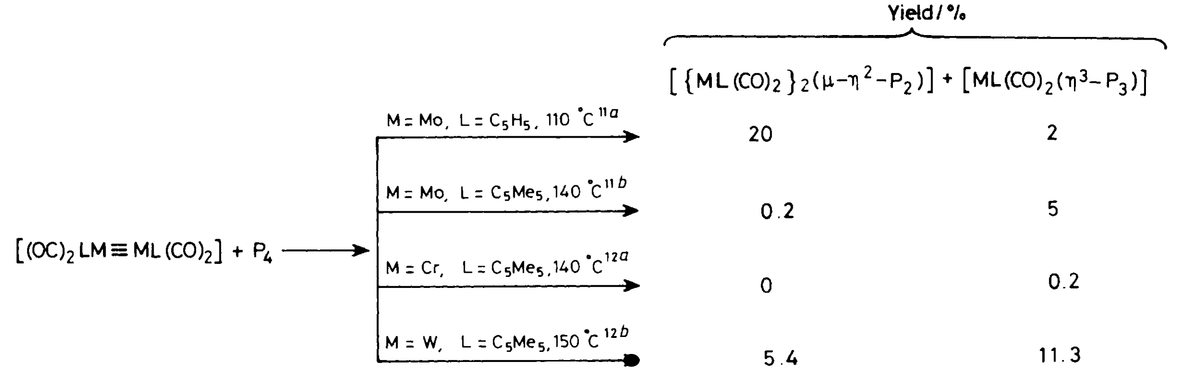
---

† μ-[Diphosphanetetrayl-P^1(Cr^{1,2})P^2(Cr^{1,2})]-bis[dicarbonyl(η-cyclopentadienyl)chromium] and dicarbonyl(η-cyclopentadienyl)(cyclotriphosphanetriyl)chromium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

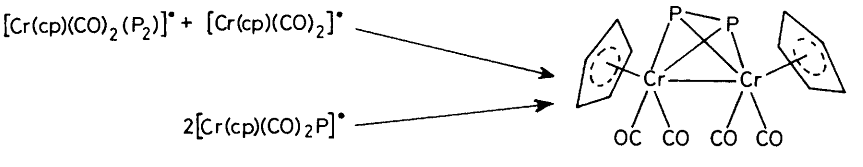
Non-S.I. unit employed: atm = 101 325 Pa.

$$[\mathrm{Co_2(CO)_8}] + \mathrm{P_4} \xrightarrow[\text{1—120 atm CO}]{\text{hexane, 10—50 °C}} [\{\mathrm{Co_3(CO)_8P}\}_3] + [\mathrm{Co_3(CO)_9P}] + [\{\mathrm{Co(CO)_3}\}_2(\mu\text{-}\eta^2\text{-}\mathrm{P_2})] + [\mathrm{Co(CO)_3}(\eta^3\text{-}\mathrm{P_3})] \tag{2}$$



(3)

$$[\{\mathrm{Cr(cp)(CO)_3}\}_2] \rightleftharpoons 2[\mathrm{Cr(cp)(CO)_3}]^{\bullet} \tag{4}$$



(1)

(5)

$$[\{\mathrm{Cr(cp)(CO)_3}\}_2] \longrightarrow [\mathrm{(OC)_2(cp)Cr{\equiv}Cr(cp)(CO)_2}] \tag{6}$$

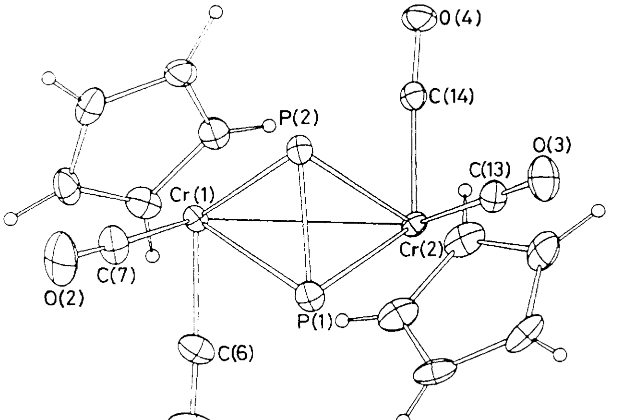


Figure 1. ORTEP drawing of $[\{\mathrm{Cr(cp)(CO)_2}\}_2(\mu\text{-}\eta^2\text{-}\mathrm{P_2})]$ (**1**)

radical-initiated reaction of P_4 with olefins,[20] and (*c*) in the formation of tetrakis(trifluoromethyl)cyclotetraphosphane from the reaction of $CF_3^{\bullet}$ radicals with white P_4.[21]

A minor contribution could come from Scherer's route [equation (3)], arising from the thermolytic decarbonylation of $[\{\mathrm{Cr(cp)(CO)_3}\}_2]$ to $[\{\mathrm{Cr(cp)(CO)_2}\}_2]$ [equation (6)],[8] which was found to occur to the extent of 10—15% under identical reaction conditions.[22]

The above findings tend to suggest that the reaction of weak or activated metal–metal bonds with elemental P_4 may be another general synthetic route to μ-η^2-P_2 and η^3-P_3 complexes, in addition to those developed by Sacconi and co-workers for the formation of η^3-P_3 complexes from the reaction of P_4 or P_4S_3, in the presence of suitable polyphosphanes, with dicationic hydrated salts of poorly co-ordinating anions[23—26] and mono- and bi-nuclear chloro complexes.[27,28]

Molecular Structures.—The ORTEP diagram for the molecular structure of $[\{\mathrm{Cr(cp)(CO)_2}\}_2\mathrm{P_2}]$ (**1**) is shown in Figure 1. Bonding parameters are given in Table 1. The molecule is isostructural with Scherer's molybdenum analogue,[11a] with a μ-η^2-P_2 ligand bridging two Cr atoms in a slightly unsymmetrical fashion, probably as a result of interligand interactions. A comparison of their unit-cell dimensions (Table 2) shows that the crystals are not isostructural. Selected bond lengths and bond angles are given in Table 3. The Cr–Cr distance of 3.011(1) Å is similar to the Mo–Mo distance [3.022(1) Å] and close to that predicted for a single bond.[13] The P–P distance in (**1**), 2.060(1) Å, agrees well with that in $[\mathrm{Co_2(CO)_6(P_2)}\{\mathrm{Cr(CO)_5}\}_2]$[29] and falls within the range [2.019(9) Å—2.154(4) Å][5] of P–P distances in μ-η^2-P_2 complexes known to date. All these values are significantly shorter than the P–P distance, 2.21 Å, in P_4 vapour.[30] Sacconi and co-workers[24,28] rationalized this finding in an analogous way as for the $[\mathrm{Co_2(CO)_6(As_2)}]$ and $[\mathrm{Co(CO)_3}(\eta^3\text{-}\mathrm{As_3})]$ complexes,[31] *viz.* the ability of the organometallic fragment(s) to act as an 'electron sink' causes a reduction in electron-pair repulsions between the P atoms, resulting in P–P bond shortening. Based on Pauling's bond length–bond order relationship,[32] the P–P bond distance of complex (**1**) corresponds to a bond order of 1.63, compared with 1.52 for the molybdenum analogue [P–P 2.079(2) Å]. These lower bond orders as compared with that of the well studied $[\mathrm{Co_2(CO)_6}(\mu\text{-}\eta^2\text{-}\mathrm{P_2})]$ and its derivative $[\mathrm{Co_2(CO)_5(PPh_3)}(\mu\text{-}\eta^2\text{-}\mathrm{P_2})]$ [P–P 2.019(9) Å equivalent to bond order 1.86] are manifested in the higher Lewis basicity of the μ-η^2-P_2 ligands.[33,34] In the presence of a Cr–Cr bond and on the assumption that the μ-η^2-P_2 ligand serves as a 4e donor, the noble gas configuration at each Cr atom is achieved.

The ORTEP view of [Cr(cp)$(CO)_2(P_3)$] (**2**) is illustrated in Figure 2. The cell dimensions (Table 2) show that the crystals are isostructural with those of the molybdenum analogue.[35] Here Cr, like Mo, is situated at the apex of a tetrahedron with an essentially equilateral basal P_3 triangle. Bond lengths and bond angles are given in Table 4. The mean P–P bond lengths of 2.125 Å compares well with equivalent bond lengths of 2.127 and 2.134 Å of the two independent molecules of the molybdenum analogue, and falls within the range, 2.115—2.159 Å, reported for mononuclear [M(tppme)(η^3-P_3)] (tppme = {$CH_3C(CH_2PPh_2)_3$}) complexes.[7] The Cr–P bond distances (average 2.452 Å) also lie within the reported range,[7] with the lowest value being observed for [Co(tppme)(η^3-P_3)] at 2.301 Å,[24] and the highest for one of the independent molecules of the molybdenum analogue at 2.538 Å.[35] The P–Cr–P angles (average 51.3°) fall near the lower end of the observed range between 49.53° (for one of the two molecules of the molybdenum analogue)[35] and 55.43° for [Co(tppme)(η^3-P_3)].[7,24] For electron-counting purposes, a 3e donation from η^3-P_3 enables Cr to attain the inert 18e configuration.

Properties and Spectral Characteristics.—Both complexes are air-stable in the solid state. They are soluble in most organic solvents, giving magenta (**1**) and yellow (**2**) solutions which are fairly stable at room temperature under an inert atmosphere. A toluene solution of (**1**) shows i.r. ν(CO) stretching frequencies at 1 970s (sh), 1 950vs, 1 925s (sh), and 1 890vs cm^{-1} as compared with ν(CO) 1 965s and 1 913s cm^{-1} for [$Mo_2(cp)_2(CO)_4(P_2)$],[11a] 1 980s, 1 920s, 1 905s, and 1 829s cm^{-1} for [$Mo_2(C_5Me_5)_2(CO)_4(P_2)$],[11b] and 1 978s, 1 915s, and 1 820m cm^{-1} for [$W_2(C_5Me_5)_2(CO)_4(P_2)$].[12b] The i.r. spectrum of complex (**2**) [ν(CO) at 1 975vs and 1 920vs cm^{-1} in toluene] shows a striking resemblance to those of its molybdenum analogue (1 995vs and 1 938s cm^{-1} in benzene),[11a] [$Mo(C_5Me_5)(CO)_2(P_3)$] (1 990vs and 1 938vs cm^{-1} in n-heptane),[11b] and [$W(C_5Me_5)(CO)_2(P_3)$] (1 985vs and 1 920vs cm^{-1} in n-heptane).[12b] Both (**1**) and (**2**) are diamagnetic and their n.m.r. data are compared with those of their molybdenum and tungsten analogues in Table 5. The cp rings and CO ligands of (**1**) all appear as singlets in both the ^1H and ^{13}C spectra, indicating an absence of coupling to the μ-η^2-P_2 ligand, unlike in the case of the molybdenum analogue,

Table 1. Bond lengths (Å) and bond angles (°) for [{Cr(cp)$(CO)_2$}$_2P_2$] (**1**)

Cr(2)–Cr(1)	3.011(1)	P(1)–Cr(1)	2.474(1)
P(2)–Cr(1)	2.341(1)	C(1)–Cr(1)	2.187(3)
C(2)–Cr(1)	2.173(3)	C(3)–Cr(1)	2.203(3)
C(4)–Cr(1)	2.232(2)	C(5)–Cr(1)	2.219(3)
C(6)–Cr(1)	1.857(3)	C(7)–Cr(1)	1.855(3)
P(1)–Cr(2)	2.353(1)	P(2)–Cr(2)	2.468(1)
C(8)–Cr(2)	2.174(3)	C(9)–Cr(2)	2.202(3)
C(10)–Cr(2)	2.230(3)	C(11)–Cr(2)	2.213(3)
C(12)–Cr(2)	2.187(3)	C(13)–Cr(2)	1.853(3)
C(14)–Cr(2)	1.846(2)	P(2)–P(1)	2.060(1)
C(1)–C(2)	1.405(5)	C(1)–C(5)	1.398(4)
C(2)–C(3)	1.406(5)	C(3)–C(4)	1.403(4)
C(4)–C(5)	1.402(5)	C(6)–O(1)	1.152(3)
C(7)–O(2)	1.149(4)	C(8)–C(9)	1.414(5)
C(8)–C(12)	1.401(5)	C(9)–C(10)	1.403(5)
C(10)–C(11)	1.406(4)	C(11)–C(12)	1.397(5)
C(13)–O(3)	1.146(3)	C(14)–O(4)	1.149(3)
P(1)–Cr(1)–Cr(2)	49.6(1)	P(2)–Cr(1)–Cr(2)	53.1(1)
P(2)–Cr(1)–P(1)	50.6(1)	C(6)–Cr(1)–Cr(2)	88.1(1)
C(6)–Cr(1)–P(1)	73.6(1)	C(6)–Cr(1)–P(2)	123.7(1)
C(7)–Cr(1)–P(1)	79.1(1)	C(7)–Cr(1)–P(2)	86.4(1)
C(6)–Cr(1)–C(7)	89.3(1)	Cr(1)–Cr(2)–P(1)	53.2(1)
Cr(1)–Cr(2)–P(2)	49.4(1)	P(2)–Cr(2)–P(1)	50.5(1)
C(13)–Cr(2)–Cr(1)	125.6(1)	C(13)–Cr(2)–P(1)	85.9(1)
C(13)–Cr(2)–P(2)	77.7(1)	C(14)–Cr(2)–Cr(1)	88.2(1)
C(14)–Cr(2)–P(1)	123.3(1)	C(14)–Cr(2)–Cr(1)	73.1(1)
C(14)–Cr(2)–C(13)	87.2(1)	Cr(2)–P(1)–Cr(1)	77.2(1)
P(2)–P(1)–Cr(1)	61.4(1)	P(2)–P(1)–Cr(2)	67.6(1)
Cr(2)–P(2)–Cr(1)	77.5(1)	P(1)–P(2)–Cr(1)	68.1(1)
P(1)–P(2)–Cr(2)	61.9(1)	O(1)–C(6)–Cr(1)	175.4(3)
O(2)–C(7)–Cr(1)	177.6(3)	O(3)–C(13)–Cr(2)	178.4(3)
O(4)–C(14)–Cr(2)	175.3(2)		

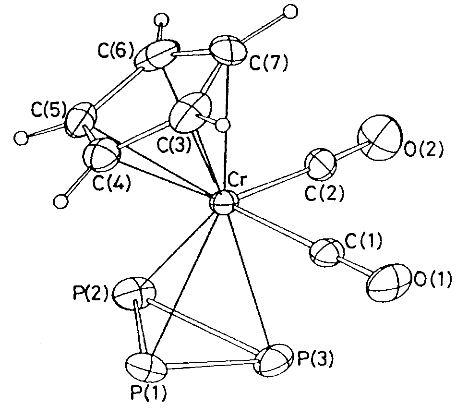


Figure 2. ORTEP drawing of [Cr(cp)$(CO)_2$(η^3-P_3)] (**2**)

Table 3. Comparison of selected bond lengths (Å) and bond angles (°) in [$M_2(cp)_2(CO)_4(P_2)$]

	M	
	Mo[11a]	Cr
P–P	2.079(2)	2.060(1)
M–M	3.022(1)	3.011(1)
P–M	2.552(1)	2.474(1), 2.468(1)
P–M′	2.463(1)	2.353(1), 2.341(1)
M–P–M′	74.1(1)	77.5(1), 77.2(1)
P–M–M′	51.6(1)	53.1(1), 49.6(1)
P–M′–M	54.3(1)	53.2(1), 49.4(1)
P–M–P′	49.01	50.5(1), 50.6(1)

Table 2. Comparison of space group (all monoclinic) and unit-cell dimensions

	[{Cr(cp)$(CO)_2$}$_2P_2$] (**1**)*	[$Mo_2(cp)_2(CO)_4(P_2)$][11a]	[Cr(cp)$(CO)_2(P_3)$] (**2**)*	[Mo(cp)$(CO)_2(P_3)$][35]
Space group	*P*2$_1$/*n*	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
a/Å	7.934(2)	13.435(2)	11.398(3)	11.459(2)
b/Å	17.189(3)	7.312(1)	14.383(1)	14.553(2)
c/Å	11.327(2)	16.971(2)	13.323(4)	13.603(1)
β/°	97.69(2)	105.44(1)	115.32(2)	115.462(9)
U/Å^3	1 530.7	1 067.0	1 974.4(5)	2 048.1(4)

* This work.

where coupling is observed in the ^{13}C spectrum.[11a] Singlet resonances are also observed in the ^{1}H and ^{13}C spectra for the cp rings and CO ligands of the η^3-P_3 complexes of Cr (**2**) and Mo. As seen in Table 5, the ^{31}P n.m.r. spectra show singlets for the μ-η^2-P_2 and η^3-P_3 ligands of (**1**) and (**2**) respectively and their corresponding molybdenum[11a] and tungsten[12b] analogues. The singlet resonance of (**1**) is found at much lower field (δ 110.76 p.p.m.) than those of its molybdenum and tungsten analogues and is little altered from that observed upon co-ordination of the μ-η^2-P_2 ligand to $Cr(CO)_5$ fragments to form $[\{Cr(cp)(CO)_2\}_2(\mu\text{-}\eta^2\text{-}P_2)\{Cr(CO)_5\}_2]$ (δ 108.4 p.p.m.).[33] The cause of this larger deshielding may be attributed to the shorter P–M bond length of (**1**), relative to that of the molybdenum analogue (Table 3). Such a trend has also been observed for the η^3-P_3 ligands of a series of $[M(tppme)(\eta^3\text{-}P_3)]$ complexes [M = Co, Rh, Ir, Ni, Pd, or Pt] in which the P–M bond length is a function of its atomic number.[26]

Table 4. Bond lengths (Å) and angles (°) for $[Cr(cp)(CO)_2(P_3)]$ (**2**)

P(1)–Cr(1)	2.436(2)	P(2)–Cr(1)	2.432(2)
P(3)–Cr(1)	2.494(2)	C(1)–Cr(1)	1.864(7)
C(2)–Cr(1)	1.864(8)	C(3)–Cr(1)	2.188(7)
C(4)–Cr(1)	2.215(7)	C(5)–Cr(1)	2.198(7)
C(6)–Cr(1)	2.164(7)	C(7)–Cr(1)	2.165(7)
P(2)–P(1)	2.126(3)	P(1)–P(3)	2.127(3)
P(2)–P(3)	2.118(3)	O(1)–C(1)	1.142(7)
C(2)–O(2)	1.140(8)	C(7)–C(3)	1.39(1)
C(3)–C(4)	1.36(1)	C(4)–C(5)	1.36(1)
C(6)–C(5)	1.39(1)	C(7)–C(6)	1.42(2)
P(4)–Cr(2)	2.427(2)	P(5)–Cr(2)	2.440(2)
P(6)–Cr(2)	2.483(2)	C(8)–Cr(2)	1.858(7)
C(9)–Cr(2)	1.860(7)	C(10)–Cr(2)	2.182(7)
C(11)–Cr(2)	2.158(7)	C(12)–Cr(2)	2.181(7)
C(13)–Cr(2)	2.198(7)	C(14)–Cr(2)	2.199(7)
P(5)–P(4)	2.135(3)	P(4)–P(5)	2.135(3)
P(6)–P(5)	2.109(3)	P(5)–P(6)	2.109(3)
O(3)–C(8)	1.145(8)	C(9)–O(4)	1.145(8)
C(14)–C(10)	1.39(1)	C(10)–C(11)	1.37(1)
C(12)–C(11)	1.43(2)	C(12)–C(13)	1.39(2)
C(14)–C(13)	1.38(2)	C(10)–C(14)	1.39(1)
P(2)–Cr(1)–P(1)	51.8(1)	P(3)–Cr(1)–P(1)	51.1(1)
P(3)–Cr(1)–P(2)	50.9(1)	C(1)–Cr(1)–P(1)	87.0(2)
C(1)–Cr(1)–P(2)	126.3(2)	C(1)–Cr(1)–P(3)	77.3(2)
C(2)–Cr(1)–P(1)	124.9(2)	C(2)–Cr(1)–P(2)	89.2(2)
C(2)–Cr(1)–P(3)	74.5(2)	C(2)–Cr(1)–C(1)	89.7(3)
P(2)–P(1)–Cr(1)	64.0(1)	P(3)–P(1)–Cr(1)	65.9(1)
P(3)–P(1)–P(2)	59.7(1)	P(1)–P(2)–Cr(1)	64.2(1)
P(3)–P(2)–Cr(1)	66.1(1)	P(3)–P(2)–P(1)	60.2(1)
P(1)–P(3)–Cr(1)	63.0(1)	P(2)–P(3)–Cr(1)	63.0(1)
P(2)–P(3)–P(1)	60.1(1)	O(1)–C(1)–Cr(1)	178.3(7)
O(2)–C(2)–Cr(1)	177.0(7)	C(7)–C(3)–C(4)	109.4(7)
C(6)–C(5)–C(4)	109.0(7)	C(7)–C(6)–C(5)	107.1(8)
C(6)–C(7)–C(3)	106.0(8)	P(5)–Cr(2)–P(4)	52.0(1)
P(6)–Cr(2)–P(4)	50.9(1)	P(6)–Cr(2)–P(5)	50.7(1)
P(5)–P(4)–Cr(2)	64.3(1)	P(6)–P(4)–Cr(2)	65.9(1)
P(6)–P(4)–P(5)	59.6(1)	P(4)–P(5)–Cr(2)	63.7(1)
P(6)–P(5)–Cr(2)	65.7(1)	P(6)–P(5)–P(4)	59.6(1)
P(4)–P(6)–Cr(2)	63.2(1)	P(5)–P(6)–Cr(2)	63.6(1)
P(5)–P(6)–P(4)	60.8(1)	C(14)–C(10)–C(11)	109.9(9)
C(12)–C(11)–C(10)	107.1(9)	C(13)–C(12)–C(11)	106(2)
C(14)–C(13)–C(12)	109.4(9)	C(13)–C(14)–C(10)	106.9(9)

It is also interesting that the deshielding effects of the μ-η^2-P_2 ligand are significantly much higher than those of η^3-P_3 for the complexes of Cr, Mo, and W studied (Table 5). The enhanced deshielding of the μ-η^2-P_2 complexes may be ascribed to the local paramagnetic contribution of Ramsey's shielding equation (7) in which the δ(paramagnetic) term is dependent upon the

$$\delta(\text{paramagnetic}) \propto -1/\langle r^3 \rangle \Delta E \qquad (7)$$

mean inverse cube of the distance between the electrons and the nucleus, the inverse of the energy separations, ΔE, between the ground and excited states, as well as the asymmetry of the electronic distribution about the nucleus. The observed shortening of the P–P bond upon complexation with the metal is indicative of greater mixing of the molecular orbitals of μ-η^2-P_2 in its bonding with the metal than of η^3-P_3, with concomitant greater reduction in the energy term ΔE. It is expected therefore that the ^{31}P resonance of μ-η^2-P_2 is found at a much lower field than that of η^3-P_3, where the M–P_3 tetrahedron is more strained than the M–P_2–M configuration. However, in the absence of accurate energy data and electronic distribution studies it is difficult to determine the exact magnitude of the downfield shift.

The parent ions of both complexes (**1**) and (**2**) are observed in their respective mass spectra which show initial stepwise cleavage of all the CO ligands before fragmentation of the μ-η^2-P_2 and η^3-P_3 units. Mass fragments arising from $Cr_2(cp)_2(P_5)$ are also observed in both spectra. In addition, the spectrum of (**1**) also shows the presence of (**2**). Indeed, these observations are in accord with the isolation of these species from the thermolytic degradation of (**1**) and (**2**).[36]

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 HE493 Dri-Train.

Reagents and Solvents.—The complex $[\{Cr(cp)(CO)_3\}_2]$ was synthesized from $[Cr(CO)_6]$ (Strem Chemicals, Inc.) by the method of Manning and co-workers.[37] Yellow phosphorus was from BDH Chemicals Ltd. Silica gel (Merck Kieselgel 60, 35—70 mesh) and Florisil (Sigma Chemical Company, 100—200

Table 5. N.m.r. data[a] of analogous μ-η^2-P_2 and η^3-P_3 complexes

Complex	^{1}H (δ)	^{13}C-$\{^{1}H\}$ (δ)	^{31}P-$\{^{1}H\}$ (δ)	Ref.
$[Cr_2(cp)_2(CO)_4(P_2)]$	4.15 (s, cp)	86.4 (s, cp), 238.60 (s, CO)	110.8	This work
$[Mo_2(cp)_2(CO)_4(P_2)]$	4.54 (s, cp)	86.5 (s, cp), 226.2 (s, CO)	−42.9	11*a*
$[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4(P_2)]$			−48.4	11*b*
$[W_2(\eta^5\text{-}C_5Me_5)_2(CO)_4(P_2)]$			−154.6	12*b*
$[Cr(cp)(CO)_2(P_3)]$	3.92 (s, cp)	84.91 (s, cp), 233.74 (s, CO)	−285.6	This work
$[Mo(cp)(CO)_2(P_3)]$	4.21 (s, cp)	85.4 (q, cp), 223.9 (q, CO)[b]	−351.5	11*a*
$[Mo(\eta^5\text{-}C_5Me_5)(CO)_2(P_3)]$			−336.5	11*b*
$[W(\eta^5\text{-}C_5Me_5)(CO)_2(P_3)]$			−381.4	12*b*

[a] In C_6D_6 at ambient temperature unless stated otherwise. Chemical shifts referenced to residual C_6H_6 for ^{1}H, to $SiMe_4$ for ^{13}C, and H_3PO_4 for ^{31}P.
[b] In CH_2Cl_2–CD_2Cl_2 at 263 K, q = quartet.

Table 6. Positional parameters (× 10^4) for complex (**1**)

Atom	x	y	z
Cr(1)	6 001(1)	1 764(1)	8 624(1)
Cr(2)	7 186(1)	383(1)	7 320(1)
P(1)	4 676(1)	1 104(1)	6 791(1)
P(2)	4 702(1)	540(1)	8 398(1)
C(1)	5 975(4)	2 021(2)	10 513(2)
C(2)	6 732(4)	2 643(2)	9 975(2)
C(3)	8 227(4)	2 368(2)	9 579(2)
C(4)	8 395(3)	1 575(2)	9 868(2)
C(5)	7 006(4)	1 367(2)	10 448(2)
C(6)	6 448(3)	2 382(1)	7 357(2)
O(1)	6 772(3)	2 801(1)	6 627(2)
C(7)	3 818(4)	2 171(2)	8 477(2)
O(2)	2 474(3)	2 429(2)	8 429(2)
C(8)	9 313(4)	−140(2)	6 588(3)
C(9)	9 964(3)	463(2)	7 366(2)
C(10)	9 266(3)	1 167(2)	6 901(2)
C(11)	8 178(4)	1 003(2)	5 846(2)
C(12)	8 234(4)	202(2)	5 652(2)
C(13)	5 886(3)	−482(1)	6 832(2)
O(3)	5 117(3)	−1 028(1)	6 531(2)
C(14)	7 714(3)	−104(1)	8 774(2)
O(4)	8 117(2)	−440(1)	9 643(2)

Table 7. Positional parameters (× 10^4) for complex (**2**)

Atom	x	y	z
Cr(1)	261(1)	6 482(1)	2 639(1)
P(1)	−916(2)	6 085(1)	3 733(2)
P(2)	192(2)	4 996(1)	3 483(2)
P(3)	1 137(2)	6 063(2)	4 645(2)
C(1)	569(7)	7 640(5)	3 333(5)
O(1)	731(6)	8 357(3)	3 738(4)
C(2)	2 042(7)	6 326(5)	3 107(6)
O(2)	3 125(6)	6 249(4)	3 350(5)
C(3)	−947(9)	7 308(5)	1 183(6)
C(4)	−1 648(7)	6 575(5)	1 227(5)
C(5)	−1 108(7)	5 776(5)	1 128(5)
C(6)	22(9)	5 995(7)	1 026(6)
C(7)	130(10)	6 978(8)	1 060(6)
Cr(2)	4 703(1)	4 020(1)	2 403(1)
P(4)	6 800(2)	3 566(2)	2 499(2)
P(5)	5 253(2)	3 642(2)	870(2)
P(6)	6 132(2)	4 867(2)	1 736(2)
C(8)	4 479(6)	5 121(5)	6 470(6)
O(3)	4 004(5)	4 599(4)	5 762(4)
C(9)	6 329(6)	5 025(5)	8 475(6)
O(4)	7 008(5)	4 446(4)	8 992(4)
C(10)	5 569(10)	6 732(6)	6 290(8)
C(11)	6 692(10)	6 281(7)	6 944(8)
C(12)	7 151(10)	6 676(7)	8 032(9)
C(13)	6 251(11)	7 346(6)	7 984(9)
C(14)	5 264(11)	7 379(6)	6 922(10)

mesh) were dried at 140 °C overnight before chromatographic use. All solvents used were distilled from sodium–benzophenone prior to use.

Physical Measurements and Elemental Analysis.—Proton and ^{13}C n.m.r. spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts referenced to residual C_6H_6 in C_6D_6 or to $SiMe_4$. The ^{31}P n.m.r. spectra were either measured on the Varian XL-200 200-MHz spectrometer at the Department of Chemistry, Texas A & M University, or a JEOL FX90Q FT 36.23-MHz spectrometer and chemical shifts referenced to external H_3PO_4. Infrared spectra were measured in the range 4 000—200 cm^{-1} by means of a Perkin-Elmer 1330 instrument, mass spectra on a Kratos AEI MS 3074. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University, or Pascher Laboratories of Bonn, Germany, except for Cr which was analysed as CrO_4^{2-} [38] in our own laboratory.

Reaction of $[\{Cr(cp)(CO)_3\}_2]$ *with* P_4.—A deep green mixture of $[\{Cr(cp)(CO)_3\}_2]$ (1.0 g, 2.48 mmol) and yellow phosphorus (0.308 g, 9.94 mmol) in toluene (20 cm^3) was stirred at *ca.* 90 °C for 3.5 h. The resultant reddish brown solution was filtered through a 2-cm disc of silica gel, eluted with toluene (5 cm^3), and concentrated to *ca.* 3 cm^3. Subsequent overnight cooling at −17 °C gave fine lustrous deep magenta crystals of $[\{Cr(cp)(CO)_2\}_2P_2]$ (**1**) (300 mg, 0.74 mmol; 30% yield). Further concentration of the mother-liquor to *ca.* 2 cm^3, followed by addition of a little n-hexane and cooling, yielded a second crop of (**1**) (120 mg, 0.29 mmol; 12% yield) (Found: C, 40.75; H, 2.55; Cr, 24.95; P, 15.15. $[\{Cr(cp)(CO)_2\}_2P_2]$ requires C, 41.2; H, 2.45; Cr, 25.45; P, 15.20%). N.m.r. (C_6D_6): ^{31}P, δ 110.76 p.p.m. Mass spectra: *m/z* 408 $[Cr_2(cp)_2(CO)_4(P_2)]$, 380 $[Cr_2(cp)_2(CO)_3(P_2)]$, 352 $[Cr_2(cp)_2(CO)_2(P_2)]$, 324 $[Cr_2(cp)_2(CO)(P_2)]$, 296 $[Cr_2(cp)_2(P_2)]$, 265 $[Cr_2(cp)_2P]$, 234 $[Cr_2(cp)_2]$, 182 $[Cr(cp)_2]$, 169 $[Cr_2(cp)]$, 148 [Cr(cp)P], and 117 (Cr(cp)]; more intense peaks at 389 $[Cr_2(cp)_2(P_5)]$ and 327 ($[Cr_2(cp)_2(P_3)]$, and peaks of comparable intensity at 266 $[Cr(cp)(CO)_2(P_3)]$, 238 $[Cr(cp)(CO)(P_3)]$, 210 $[Cr(cp)(P_3)]$, 207 $[Cr(cp)(CO)(P_2)]$, and unassigned peaks at 154 and 123.

The mother-liquor from the second crop of complex (**1**) was concentrated to *ca.* 1 cm^3 and loaded onto a column (1 × 20 cm) of Florisil prepared in n-hexane. Elution with n-hexane (50 cm^3) yielded a yellow fraction from which was obtained dark brown crystalline $[Cr(cp)(CO)_2(P_3)]$ (**2**) (525 mg, 1.97 mmol; 40% yield) {Found: C, 32.5; H, 1.95; Cr, 18.8; P, 32.65. $[Cr(cp)(CO)_2(P_3)]$ requires C, 31.6; H, 1.90; Cr, 19.55; P, 34.95%). N.m.r. (C_6D_6): ^{31}P, δ −285.58 p.p.m. Mass spectrum: *m/z* 266 $[Cr(cp)(CO)_2(P_3)]$, 262 $[Cr_2(cp)(P_3)]$, 238 $[Cr(cp)(CO)(P_3)]$, 210 $[Cr(cp)(P_3)]$, 182 $[Cr(cp)_2]$, 148 [Cr(cp)P], 145 $[Cr(P_3)]$, 117 (Cr(cp)], higher mass fragments 420 $[Cr_2(cp)_2(P_6)]$, 389 $[Cr_2(cp)_2(P_5)]$, 358 $[Cr_2(cp)_2(P_4)]$, and 327 $[Cr_2(cp)_2(P_3)]$, and an unassigned peak at 180. Further elution with n-hexane–toluene (1:1) (30 cm^3) gave a magenta fraction from which was obtained more of (**1**) (115 mg, 0.28 mmol; 11% yield).

Crystal Structure Determinations.—Single crystals of complexes (**1**) and (**2**) were obtained as dark magenta cuboid diamond-shaped crystals and dark brown needles, respectively, from n-hexane–toluene, after *ca.* 10 d at −28 °C.

Crystal data. (**1**), $C_{14}H_{10}Cr_2O_4P_2$, $M = 408.2$, monoclinic, space group $P2_1/n$, $a = 7.934(2)$, $b = 17.189(3)$, $c = 11.327(2)$ Å, $\beta = 97.69(2)°$, $D_c = 1.771$ g cm^{-3}, $U = 1\,530.7$ Å^3, $Z = 4$, $F(000) = 816$, $\mu(Mo\text{-}K_\alpha) = 15.63$ cm^{-1}, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å.

(**2**), $C_7H_5CrO_2P_3$, $M = 266.0$, monoclinic, space group $P2_1/c$, $a = 11.398(3)$, $b = 14.383(1)$, $c = 13.323(4)$ Å, $\beta = 115.32(2)°$, $D_c = 1.789$ g cm^{-3}, $U = 1\,974.4(5)$ Å^3, $Z = 8$, $F(000) = 1\,056$, $\mu(Mo\text{-}K_\alpha) = 15.16$ cm^{-1}, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å.

Reflections were measured ($2° < 2\theta < 50°$) on an Enraf-Nonius CAD4-F four-circle diffractometer, 3 093 reflections being collected for (**1**) and 3 819 for (**2**). The structures were solved by direct methods and refined to R values of 0.026 on 2 446 observed reflections [$I > 2.5\sigma(I)$] for (**1**) and 0.048 on 2 089 [$I > 2.5\sigma(I)$] for (**2**); weighting schemes, $w = 2.26/(\sigma^2F_o + 0.000\,27\ F_o^2)$ and $2.26/(\sigma^2F_o + 0.000\,47\ F_o^2)$ respectively. Program used was SHELX 76.[39] Positional parameters are listed in Tables 6 and 7, selected bond lengths and bond angles in Tables 1 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Acknowledgements

Support from the University of Malaya and The University of Sydney is gratefully acknowledged. The authors also thank the Department of Chemistry (in particular Professor D. J. Darensbourg), Texas A and M University and the Palm Oil Research Institute of Malaysia for the ^{31}P n.m.r. spectra.

References

1 H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 379 and refs. therein.
2 D. A. Roberts and G. L. Geoffroy, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, ch. 40 and refs. therein.
3 L. Y. Goh, T. W. Hambley, and G. B. Robertson, *J. Chem. Soc., Chem. Commun.*, 1983, 1458; *Organometallics*, 1987, **6**, 1051.
4 L. Y. Goh, Chen Wei, and E. Sinn, (*a*) *J. Chem. Soc., Chem. Commun.*, 1985, 462; (*b*) *Organometallics*, 1988, **7**, 2020.
5 M. Di Varia, P. Stoppioni, and M. Peruzzini, *Polyhedron*, 1987, **6**, 351 and refs. therein.
6 O. J. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 924 and refs. therein.
7 M. Di Varia and L. Sacconi, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 330 and refs. therein.
8 P. Hackett, P. S. O'Neill, and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1974, 1625.
9 L. Y. Goh, M. J. D'Aniello, jun., S. Slater, E. L. Muetterties, I. Tavanaiepour, M. I. Chang, M. F. Fredrich, and V. W. Day, *Inorg. Chem.*, 1979, **18**, 192.
10 A. Vizi-Orosz, G. Pályi, and L. Markó, *J. Organomet. Chem.*, 1973, **60**, C25; 1976, **111**, 61.
11 O. J. Scherer, H. Sitzmann, and G. Wolmershäuser, (*a*) *J. Organomet. Chem.*, 1984, **268**, C9; (*b*) *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 351.
12 (*a*) O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim, and R. Groß, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 363; (*b*) O. J. Scherer, J. Schwalb, H. Swarowsky, G. Wolmershäuser, W. Kaim, and R. Gross, *Chem. Ber.*, 1988, **121**, 443.
13 R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Am. Chem. Soc.*, 1974, **96**, 749.
14 S. J. McLain, *J. Am. Chem. Soc.*, 1988, **110**, 643 and refs. therein.
15 B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, 1975, **79**, 947; D. R. Kidd and T. L. Brown, *ibid.*, 1978, **100**, 4095.
16 (*a*) N. A. Cooley, K. A. Watson, S. Fortier, and M. C. Baird, *Organometallics*, 1986, **5**, 2563 and refs. therein; (*b*) J. M. Hanckel, K-W. Lee, P. Rushman, and T. L. Brown, *Inorg. Chem.*, 1986, **25**, 1852 and refs. therein; (*c*) T. J. Meyer and J. V. Caspar, *Chem. Rev.*, 1985, **85**, 187 and refs. therein.
17 M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, 1975, **97**, 2065; D. S. Ginley, C. R. Bock, and M. S. Wrighton, *Inorg. Chim. Acta*, 1977, **23**, 85 and refs. therein.
18 M. Grayson, *Pure Appl. Chem.*, 1964, **9**, 193 and refs. therein.
19 D. Perner and A. Henglein, *Z. Naturforsch., Teil B*, 1962, **17**, 703.
20 W. E. Garwood and L. A. Hamilton, U.S.P., 2 731 458/1956; W. E. Garwood, L. A. Hamilton, and F. M. Seger, *Ind. Eng. Chem.*, 1960, **52**, 401.
21 W. H. Watson, *Tex. J. Sci.*, 1959, **11**, 471.
22 L. Y. Goh and R. C. S. Wong, unpublished work.
23 M. Di Vaira, C. A. Ghilardi, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, 1978, **100**, 2550.
24 C. A. Ghilardi, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1980, **19**, 301.
25 F. Cecconi, P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 3292.
26 M. Di Vaira, L. Sacconi, and P. Stoppioni, *J. Organomet. Chem.*, 1983, **250**, 183.
27 C. Bianchini, C. Mealli, A. Meli, and L. Sacconi, *Inorg. Chim. Acta*, 1979, **37**, L543.
28 P. Dapporto, L. Sacconi, P. Stoppioni, and F. Zanobini, *Inorg. Chem.*, 1981, **20**, 3834.
29 H. Lang, L. Zsolnai, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 976.
30 L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, 1935, **3**, 699.
31 A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Am. Chem. Soc.*, 1969, **91**, 5631, 5633.
32 L. Pauling, 'The Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960, p. 239.
33 L. Y. Goh, T. C. W. Mak, and R. C. S. Wong, *J. Organomet. Chem.*, 1989, **364**, 363.
34 O. J. Scherer, H. Sitzmann, and G. Wolmershauser, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 968.
35 O. J. Scherer, H. Sitzmann, and G. Wolmershauser, *Acta Crystallogr., Sect. C*, 1985, **41**, 1761.
36 L. Y. Goh, R. C. S. Wong, T. C. W. Mak, C. K. Chu and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, in the press.
37 R. Birdwhistell, P. Hackett, and A. R. Manning, *J. Organomet. Chem.*, 1978, **157**, 239.
38 G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 414.
39 G. M. Sheldrick, SHELX 76, Crystal Structure Solving Package, University of Cambridge, 1976.

Received 6*th December* 1988; *Paper* 8/04813D