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Coordination of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ to metal carbonyl fragments and crystal structure of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$

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Abstract

$Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (I) reacts with 2 mole equivalents of $M(CO)_5THF$ to give $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[M(CO)_5]_2$ (M = Cr, II; Mo, III; W, IV) in 65–70% yields. The reaction with 1 mole equivalent of $Cr(CO)_5THF$ gave the mono-metallated complex $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]$ (V) in 60% yield along with II in 18% yield. In the presence of stoichiometric amount of PPh_3 as a $Cr(CO)_5$ scavenger, II was converted into V and I. X-ray analysis showed that II has C_2 molecular symmetry; the Cr–Cr′ and P–P′ bond distances in the tetrahedral Cr_2P_2 core are 3.003(1) and 2.063(1) Å, respectively.

Introduction

The last few years have witnessed an upsurge of interest in the chemistry of transition metal complexes containing mono- to quadri-atomic units of phosphorus as ligands [1,2]. Since the first discovery by Markó and Vizi-Orosz in 1973 [3a] (see also [3b]) of a $\mu\text{-}\eta^2\text{-}P_2$ complex, $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2)$, in which P_2 functions as a side-on bonded 4e-donor ligand, followed by the structural determination of its triphenylphosphine derivative, $Co_2(CO)_5(PPh_3)(\mu\text{-}\eta^2\text{-}P_2)$ in 1979 [4], similar M_2P_2 complexes have been prepared for Mo [5], W [6], Ni [7], and more recently, in our laboratory, for Cr [8]. Except for a recent report on an extended Hückel treatment of the geometrical forms of $Co_2(CO)_6P_2$ and related complexes [9], the emphasis so far has been on their structural characterisation. There have been only a few studies of the reactions of these complexes, the main contribution coming largely from the work of Pályi and Markó on the carbonyl substitution [10] and the Lewis acid/base

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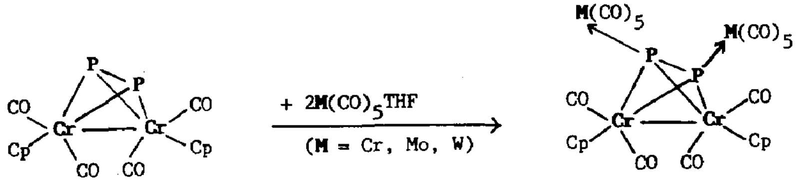
behaviour [11,12] of $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2)$. Recently, Scherer succeeded in bringing about coordination of the lone electron pairs of the P_2 unit of $Cp_2Mo_2(CO)_4P_2$ to substitution-labile metal carbonyl complexes such as $Cr(CO)_5THF$ and $Re_2(CO)_6(\mu\text{-}Br)_2(THF)_2$ [13]. Having available $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ [8], we decided to carry out related studies on it for purposes of comparison. Our findings are reported below.

Results and discussion

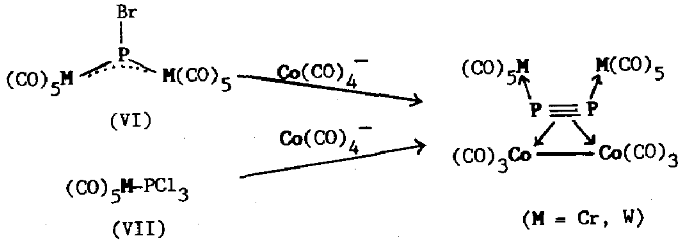
Reaction with metal carbonyl fragments

$Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (I) reacts readily at ambient temperature with 1 molar equivalent of $Cr(CO)_5(THF)$ to give the mono-metallated complex $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]$ (V) and the di-metallated complex $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II) in 60 and 18% yields, respectively. With 2 molar equivalents of $Cr(CO)_5(THF)$, only II was obtained, in 51% isolated yield, as air-stable dark brown rhomboidal crystals. Likewise, the reaction with 2 molar equivalents of $Mo(CO)_5(THF)$ and $W(CO)_5(THF)$ gave $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Mo(CO)_5]_2$ (III) and $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[W(CO)_5]_2$ (IV) as air-stable dark reddish brown trapezoidal crystals and dark greenish brown rectangular plates in 69.5 and 65% yields, respectively. It appears that the facile coordination of the ligated $\mu\text{-}\eta^2\text{-}P_2$ unit to additional transition metal carbonyl fragments is a common feature of Group VI dinuclear $Cp_2M_2(CO)_4P_2$ complexes (eq. 1).



(1)

Recently Scherer observed the first example of this in the reactions of $Cp_2Mo_2(CO)_4P_2$ with $Cr(CO)_5(THF)$ and $Re(CO)_6(\mu\text{-}Br)_2(THF)_2$ [13]. It is noteworthy that the $\mu\text{-}\eta^2\text{-}P_2$ unit of the well-studied $Co_2(CO)_6P_2$ complex cannot be made to coordinate in this manner [11]. Thus, $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2)[M(CO)_5]_2$ (M = Cr, W) can only be synthesised from the reaction of halophosphanediyl complexes (VI) or halophosphane complexes (VII) with tetracarbonylcobaltate (eq. 2) [14].

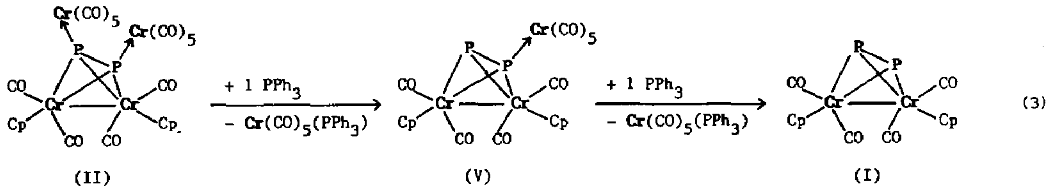


(2)

We believe that the coordinating ability of the P_2 entity in I and the analogous Mo complex [13], which is an indication of its higher Lewis basicity compared with that in $Co_2(CO)_6P_2$, is associated with the longer P–P bond distances (2.060 Å for M = Cr (see Table 3) and 2.079 Å for M = Mo [5a]), compared with the value of 2.019 Å in $Co_2(CO)_6P_2$ [4] and hence lower bond orders (1.63, 1.52 and 1.86, respectively, for Cr, Mo, and Co) [15].

Reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II) with PPh_3

By means of diagnostic TLC, it was demonstrated that PPh_3 will abstract a molar equivalent of the metal carbonyl fragment $Cr(CO)_5$ from a 1 *M* solution of II in THF to give V, and eventually I [$R_f = 0.15$, 0.42 and 0.61 respectively in 3/6/1 n-hexane/toluene/THF], after 9 h at 60 °C (eq. 3).



(3)

Such a reaction sequence has been reported for the Mo and W diarsenic complexes $Cp_2M_2(CO)_4As_2[Cr(CO)_5]_2$ [16].

Structure of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II)

The molecule has crystallographic C_2 symmetry, and each P atom of the side-on bonded $\mu\text{-}\eta^2\text{-}P_2$ unit of the tetrahedral Cr_2P_2 core is linked to a $Cr(CO)_5$ fragment (see Fig. 1). Atomic coordinates and thermal parameters are given in Table 1, and bond lengths and selected bond angles in Table 2.

The structure shows a close resemblance to that of $Co_2(CO)_6(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ [14], with very close agreement between the values of the P–P bond distance [Δ 0.003 Å]. As in the case of the Co complex, there is little difference between the core unit of II and that of its parent compound (I) [8], as is apparent from comparison of some bond lengths and bond angles given in Table 3. The $Mo(CO)_5$ and $W(CO)_5$ analogues are isostructural with the bis-$Cr(CO)_5$ complex II, in space group $C2/c$, and their cell dimensions are compared in Table 4. In addition to the $M_2(\mu\text{-}\eta^2\text{-}P_2)M'_2$ complexes discussed above, the only other known example is $[Fe(CO)_3]_2(\mu\text{-}CO)P_2[Cr(CO)_5]_2$, which has a P–P bond distance 2.087 Å, prepared from the reaction of $Fe_2(CO)_9$ and $(CO)_5CrPBr_3$ [17].

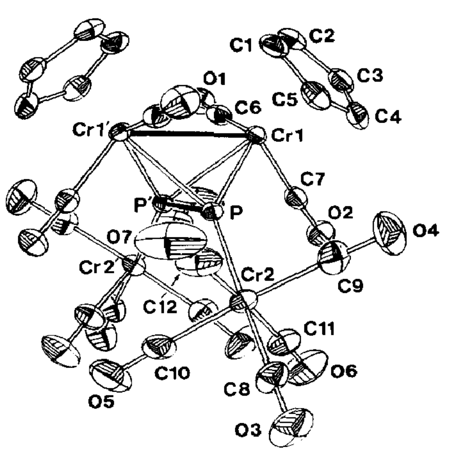


Fig. 1. Perspective view of the $Cr_2Cp_2(CO)(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ molecule (II), whose C_2 symmetry axis passes through the mid-points of the Cr(1)–Cr(1′) and P–P′ bonds. The thermal ellipsoids are drawn at the 35% probability level.

Table 1

Atomic coordinates ($\times 10^5$ for Cr and P atoms; $\times 10^4$ for other atoms) and thermal parameters [a] ($Å^2 \times 10^4$ for Cr and P atoms; $\times 10^3$ for other atoms)

Atom	x	y	z	U_{eq}/U
Cr(1)	51803(2)	24389(3)	16943(2)	394(2)
Cr(2)	34171(2)	55482(4)	15182(2)	295(2)
P	44321(3)	39814(5)	20885(3)	284(2)
C(1)	4481(2)	597(3)	1422(2)	59(1)
C(2)	5186(2)	393(2)	1292(2)	59(1)
C(3)	5223(2)	1235(3)	646(2)	58(1)
C(4)	4525(2)	1957(3)	368(2)	59(1)
C(5)	4072(2)	1564(3)	854(2)	59(1)
C(6)	6206(1)	2050(2)	2348(2)	46(1)
O(1)	6833(1)	1769(2)	2729(2)	69(1)
C(7)	5535(2)	3809(2)	1186(2)	46(1)
O(2)	5744(2)	4624(2)	858(1)	72(1)
C(8)	2633(2)	6769(3)	1060(2)	62(1)
O(3)	2145(2)	7507(3)	782(2)	99(1)
C(9)	3081(2)	4622(3)	471(2)	64(1)
O(4)	2877(2)	4104(3)	−166(2)	103(1)
C(10)	3752(2)	6542(3)	2533(2)	67(1)
O(5)	3935(2)	7187(3)	3112(2)	119(1)
C(11)	4076(2)	6560(3)	1109(2)	59(1)
O(6)	4443(2)	7207(3)	852(2)	102(1)
C(12)	2707(2)	4652(3)	1916(3)	75(1)
O(7)	2255(2)	4187(3)	2144(3)	143(2)
H(1)	4297(19)	247(32)	1757(23)	80
H(2)	5561(17)	−161(32)	1577(21)	80
H(3)	5613(19)	1365(33)	446(22)	80
H(4)	4374(21)	2554(33)	−49(23)	80
H(5)	3595(20)	1839(33)	782(21)	80

[a] For non-hydrogen atoms, the equivalent isotropic temperature factor U_{eq} is defined as 1/3 of the trace of the orthogonalised U matrix. For H atoms, the exponent of the temperature factor expression takes the form $-8\pi^2 U \sin^2\theta/\lambda^2$.

The formation of these homo- and hetero-bimetallated derivatives of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ complements Scherer's demonstration of the donor ability of the P_2 ligand in $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ [13].

Experimental

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

All solvents used were distilled from sodium/benzophenone prior to use. $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ was synthesized from $Cp_2Cr_2(CO)_6$ [8]. Silica gel (Merck Kieselgel 60, 35–70 mesh) and Florisil (Sigma, 100–200 mesh) were dried at 140 °C overnight before chromatographic use.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX100 spectrometer and chemical shifts are relative to $(CH_3)_4Si$. ^{31}P spectra were recorded on a JEOL FX90Q FT spectrometer (36.23 MHz), and chemical shifts are relative to external

Table 2

Bond lengths (Å) and selected bond angles (°) [a]

Cr(1)–Cr(1′)	3.003(1)	Cr(1)–P	2.340(1)	Cr(1)–P′	2.489(1)
P–P′	2.063(1)	Cr(1)–C(1)	2.245(3)	Cr(1)–C(2)	2.210(3)
Cr(1)–C(3)	2.176(3)	Cr(1)–C(4)	2.191(2)	Cr(1)–C(5)	2.224(3)
Cr(1)–C(6)	1.864(2)	Cr(1)–C(7)	1.878(3)	C(1)–C(2)	1.402(5)
C(2)–C(3)	1.407(4)	C(3)–C(4)	1.412(4)	C(4)–C(5)	1.414(5)
C(5)–C(1)	1.401(4)	C(6)–O(1)	1.143(3)	C(7)–O(2)	1.141(4)
Cr(2)–P	2.397(1)	Cr(2)–C(8)	1.863(3)	Cr(2)–C(9)	1.905(3)
Cr(2)–C(10)	1.898(3)	Cr(2)–C(11)	1.897(3)	Cr(2)–C(12)	1.898(4)
C(8)–O(3)	1.143(4)	C(9)–O(4)	1.137(4)	C(10)–O(5)	1.128(4)
C(11)–O(6)	1.133(5)	C(12)–O(7)	1.132(6)		
Cr(1)–P–Cr′(1′)	76.9(1)	Cr(1)–P–P′	68.5(1)	Cr(1)–P–Cr(2)	142.5(1)
Cr(1′)–P–Cr(2)	135.8(1)	Cr(2)–P–P′	137.1(1)	Cr(1′)–P–P′	61.0(1)
P–Cr(1)–Cr(1′)	53.8(1)	P–Cr(1)–P′	50.5(1)	P′–Cr(1)–Cr(1′)	49.3(1)
P–Cr(1)–C(6)	123.4(1)	P–Cr(1)–C(7)	87.2(1)	P′–Cr(1)–C(6)	73.2(1)
P′–Cr(1)–C(7)	81.4(1)	Cr(1′)–Cr(1)–C(6)	87.8(1)	Cr(1′)–Cr(1)–C(7)	129.1(1)
C(6)–Cr(1)–C(7)	89.4(1)	Cr(1)–C(6)–O(1)	177.2(2)	Cr(1)–C(7)–O(2)	178.2(2)
P–Cr(2)–C(8)	179.1(1)	P–Cr(2)–C(9)	89.5(1)	P–Cr(2)–C(10)	92.2(1)
P–Cr(2)–C(11)	90.5(1)	P–Cr(2)–C(12)	93.8(1)	C(8)–Cr(2)–C(9)	90.0(1)
C(8)–Cr(2)–C(10)	88.3(1)	C(8)–Cr(2)–C(11)	88.8(1)	C(8)–Cr(2)–C(12)	86.9(1)
C(9)–Cr(2)–C(10)	177.4(1)	C(9)–Cr(2)–C(11)	89.0(1)	C(9)–Cr(2)–C(12)	92.4(2)
C(10)–Cr(2)–C(11)	89.0(1)	C(10)–Cr(2)–C(12)	89.6(2)	C(11)–Cr(2)–C(12)	175.5(1)
Cr(2)–C(8)–O(3)	179.1(3)	Cr(2)–C(9)–O(4)	178.0(3)	Cr(2)–C(10)–O(5)	176.5(3)
Cr(2)–C(11)–O(6)	176.8(3)	Cr(2)–C(12)–O(7)	175.6(3)		

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[a] The primed atoms are generated by the symmetry transformation $(1-x,\ y,\ 1/2-z)$.

Table 3

A comparison of selected bond lengths and bond angles in $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ and its parent compound I

	$Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (I) [a]	$Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II)
Cr(1)–Cr(1′)	3.011(1)	3.003(1)
P–P′	2.060(1)	2.063(1)
Cr(1)–P	2.341(1)	2.340(1)
Cr(1)–P′	2.474(1)	2.489(1)
Cr(1′)–P	2.468(1)	2.489(1)
Cr(1′)–P′	2.353(1)	2.340(1)
Cr(1′)–Cr(1)–P	53.1(1)	53.8(1)
Cr(1′)–Cr(1)–P′	49.6(1)	49.3(1)
Cr(1)–Cr(1′)–P	49.4(1)	49.3(1)
Cr(1)–Cr(1′)–P′	53.2(1)	53.8(1)
Cr(1)–P–Cr(1′)	77.5(1)	76.9(1)
Cr(1)–P′–Cr(1′)	77.2(1)	76.9(1)
P′–Cr(1)–P	50.6(1)	50.5(1)
P′–Cr(1′)–P	50.5(1)	50.5(1)

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[a] From reference 8.

Table 4

Unit-cell dimensions of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[M(CO)_5]_2$

M	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Cr	18.361(2)	10.281(2)	16.806(4)	110.34(2)	2975(1)
Mo	18.553(5)	10.462(2)	16.786(1)	109.84(1)	3064.5(8)
W	18.552(6)	10.471(2)	16.768(2)	109.77(2)	3065(1)

$P(OMe)_3$ [δ 140.67 to external H_3PO_4]. IR spectra were recorded on a Perkin–Elmer 1330 instrument. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University and the Pascher Laboratories in Bonn, Germany, except for Cr, which we determined as CrO_4^{2-} [18].

X-Ray structural analysis

Diffraction data were collected on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, $\lambda = 0.71069$ Å), and determination of the crystal class, orientation matrix, and accurate unit-cell parameters were carried out by standard procedures [19]. Intensities were recorded at 22°C, and data

Table 5

Data collection and processing parameters for $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II)

Molecular formula	$C_{24}H_{10}O_{14}P_2Cr_4$	
Molecular weight	792.28	
Cell constants	a 18.361(2) Å	β 110.34(2)°
	b 10.281(2) Å	V 2975(1) Å^3
	c 16.806(4) Å	$Z = 4$
		$F(000) = 1567.8$
Density (exp.)	1.784 g cm^{-3} (flotation in $CCl_4/BrCH_2CH_2Br$)	
Density (calc)	1.769 g cm^{-3}	
Space group	$C2/c$	
Radiation	graphite-monochromatized Mo-K_α, λ 0.71069 Å	
Absorption coefficient	15.60 cm^{-1}	
Crystal size	0.50×0.40×0.20 mm	
Mean μ_r	0.248	
Transmission factors	0.578 to 0.693	
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}	
Scan range	1° below K_{α_1} to 1° above K_{α_2}	
Background counting	stationary counts for one-half of scan time at each end of scan range	
Collection range	$h, k, \pm l$; $2\theta_{max} = 60°$	
Unique data measured	3902	
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$, n	3390	
Number of variables, p	214	
$R = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$	0.046	
Weighting scheme	$w = [\sigma^2(\lvert F_o \rvert) + 0.0008 \lvert F_o \rvert^2]^{-1}$	
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.049	
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / (n - p)]^{1/2}$	1.147	
Residual extrema in final difference map	+0.49 to −0.41 eÅ^{-3}	

collection and processing parameters are summarized in Table 5. The raw intensities were processed by the learnt-profile procedure [20], and absorption correction was based on a pseudo-ellipsoidal fit to azimuthal scans of selected strong reflections over a range of 2θ values [21,22].

The structure was revealed by a sharpened Patterson function. All non-hydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The cyclopentadienyl hydrogen atoms were located from a difference map, and allowed to vary with their assigned isotropic temperature factors held constant. All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system [23]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [24]. Blocked-cascade least-squares refinement [25] converged to the R indices and other parameters listed in Table 5.

The final atomic coordinates are listed in Table 1. Selected bond distances and bond angles are given in Table 2. A table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

Preparation of $M(CO)_5THF$ solutions

Solutions of $M(CO)_5(THF)$ (M = Cr, Mo, W) (0.007 M) were prepared from $M(CO)_6$ in THF as described by Strohmeier et al. [26].

Reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ with $Cr(CO)_5(THF)$

(a) At 1/2 molar ratio. A solution of $Cr(CO)_5(THF)$ (24 ml, 0.168 mmol) was injected into a magenta solution of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (30 mg, 0.074 mmol) in THF (5 ml), and the mixture was stirred at ambient temperature. After 30 min the solution had turned yellowish brown. Stirring was continued for a further 1.5 h and the solution was then concentrated to dryness, the residue redissolved in ca. 1 ml toluene, and the solution placed on a silica gel column (1 × 10 cm) prepared in n-hexane. Two fractions were collected: (i) a yellow fraction in n-hexane (5 ml), which on dryness gave unchanged $Cr(CO)_5(THF)$ (ca. 8 mg); and (ii) a yellowish brown solution eluted with toluene (20 ml) followed by 4/1 toluene/THF (5 ml), which on concentration to ca. 2 ml and slow crystallisation at room temperature yielded air-stable dark brown rhomboidal crystals of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II) suitable for X-ray analysis (30 mg, 0.038 mmol, 51% yield). The mother liquor contained ca. 10 mg (17% yield) of the product. Anal. Found: C, 35.89; H, 1.22; P, 8.03; Cr, 25.90. $C_{24}H_{10}O_{14}P_2Cr_4$ calc: C, 36.38; H, 1.27; P, 7.82; Cr, 26.24%. IR(THF): ν(CO) 2070s, 2060s, 1980vs, 1931vs cm^{-1}. ^1H NMR (30 °C): δ(Cp) 4.12 (C_6D_6), 4.21 ($C_6D_6CD_3$). ^{13}C NMR (C_6D_6, 30 °C) δ(Cp) 87.91 and ($C_6D_5CD_3$, −70 °C): δ(Cp) 87.40; δ(CO) 215.5, 221.1, 229.3, 271.6, 272.6, 276.5, 280.1, 281.1, 282.0, 283.0, 283.9, 284.9, 285.8, 286.7. ^{31}P NMR (C_6D_6, 30 °C): δ 108.36.

(b) At 1/1 molar ratio. The procedure described above was repeated for $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (28 mg, 0.069 mmol) and $Cr(CO)_5(THF)$ (9.8 ml, 0.069 mmol). Similar work-up of the resulting reddish brown solution, but with use of a Florisil column (1 × 10 cm), gave 4 fractions: (i) a green n-hexane solution (ca. 5 ml) which gave a green uncharacterised residue (2 mg); (ii) a magenta solution, in 1/9 toluene/n-hexane (15 ml), of unchanged I (4 mg, 0.0098 mmol, 14.2%); (iii) a

reddish brown solution in 3/5 toluene/n-hexane, which gave fine dark crystalline solids of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]$ (V) (25 mg, 0.042 mmol, 60% yield), and finally (iv) a greenish brown solution obtained by elution with toluene (10 ml) followed by 1/1 toluene/ether (20 ml), which gave fine dark brown crystals of II (10 mg, 0.013 mmol, 18% yield). Anal. Found: C, 38.20; H, 1.72; P, 10.91; Cr, 25.92. $C_{19}H_{10}O_9P_2Cr_3$ calc: C, 38.02; H, 1.68; P, 10.32; Cr, 25.99%. IR(THF): ν(CO) 2054m, 1967vs, 1935vs, 1909ssh cm^{-1}. ^1H NMR (C_6D_6, 30 °C): δ(Cp) 4.14. ^{13}C NMR (C_6D_6, 30 °C): δ(Cp) 87.30, δ(CO) 236.6, 236.4, 236.2, 236.0, 216.7, 216.5, 216.3, 215.9, 215.7.

Reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ with $Mo(CO)_5(THF)$

The procedure described above was repeated for a solution of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (60 mg, 0.147 mmol) in THF (5 ml) and $Mo(CO)_5(THF)$ (0.007 *M*, 44 ml). Chromatography of the reddish brown product solution on a silica gel column (1 × 15 cm) gave 2 fractions: (i) a yellow solution in n-hexane (5 ml), which gave $Mo(CO)_5(THF)$ (ca. 5 mg), and (ii) a reddish brown solution eluted with toluene (15 ml) and then 4/1 toluene/THF (15 ml), which on concentration to ca. 3 ml and slow crystallisation at room temperature gave air-stable dark reddish-brown trapezoidal crystals of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Mo(CO)_5]_2$ (80 mg, 0.091 mmol, 62% yield). Addition of n-hexane (ca. 0.3 ml) to the mother liquor gave a second crop (10 mg, 0.011 mmol, 7.5% yield). Anal. Found: C, 33.06; H, 1.10, P, 6.81; Cr, 12.08; Mo, 17.30. $C_{24}H_{10}O_{14}P_2Cr_2Mo_2$ calc: C, 32.74; H, 1.15; P, 7.04; Cr, 11.81; Mo, 21.81%. IR(THF): ν(CO) 2080s, 2070s, 1980vs, 1935vs cm^{-1}. ^1H NMR (C_6D_6, 30 °C): δ(Cp) 4.11. ^{13}C NMR (C_6D_6, 30 °C): δ(Cp) 87.89.

Reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ with $W(CO)_5(THF)$

A mixture of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (50 mg, 0.123 mmol) in THF (5 ml) and $W(CO)_5(THF)$ (0.007 *M*, 42 ml) was kept for 4–5 h at ambient temperature. The resulting greenish brown solution was worked up as described above. Two chromatographic fractions were obtained: (i) a yellow solution of unreacted $W(CO)_5(THF)$ (ca. 10 mg residue), and (ii) a greenish brown solution which yielded a first crop of air-stable dark greenish brown thick rectangular plates (75 mg, 0.071 mmol, 58% yield) followed by a second crop (10 mg, 0.009 mmol, 7.3% yield). Anal. Found: C, 27.27; H, 0.97; P, 5.71; Cr, 9.11; W, 33.80. $C_{24}H_{10}O_{14}P_2Cr_2W_2$ calc: C, 27.28; H, 0.96; P, 5.87; Cr, 9.84; W, 34.83%. IR(THF): ν(CO) 2065s, 2058s, 1980vs, 1928vs cm^{-1}. ^1H NMR (C_6D_6, 30 °C): δ(Cp) 4.10. ^{13}C NMR (C_6D_6, 30 °C): δ(Cp) 87.96.

Reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (II) with PPh_3

Solutions of II (1 mg, 0.00126 mmol) in THF (1 ml) were treated with PPh_3 (a) (0.332 mg, 0.00126 mmol); (b) (0.664 mg, 0.00252 mmol) and (c) (3.32 mg, 0.0126 mmol) at 60 °C for 9 h. Spots of the product solutions were then placed on Merck Kieselgel plates and eluted with a mixture of 3/6/1 n-hexane/toluene/THF. The chromatogram for (a) showed mainly $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]$ (V) (R_f 0.42) and a trace of unchanged II (R_f 0.15); (b) showed mainly $Cp_2Cr_2(CO)_4P_2$ (I) (R_f 0.61), with a trace of unchanged II and some V; (c) showed the presence of only I.

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