

# Coordination of the ( $\mu\text{-}\eta^2\text{-As}_2$ ) ligand to Group 6 transition metal carbonyl fragments and crystal structures of $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{As}_2[\text{M}(\text{CO})_5]_2$ ( $\text{M} = \text{Cr}, \text{W}$ )

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## Abstract

$[\text{CpCr}(\text{CO})_2]_2(\mu\text{-}\eta^2\text{-As}_2)$  (**1**) reacts with 2 mol equiv. of  $\text{M}(\text{CO})_5(\text{THF})$  to give the adducts  $[\text{CpCr}(\text{CO})_2]_2(\mu\text{-}\eta^2\text{-As}_2)[\text{M}(\text{CO})_5]_2$  (**2A**,  $\text{M} = \text{Cr}$ ; **2B**,  $\text{M} = \text{W}$ ) in 55–60% isolated yields. The adducts are isostructural, possessing a crystallographic  $C_2$  axis through the midpoints of the As–As and Cr–Cr bonds. Bonding parameters are indicative of a small degree of steric effects imposed by the coordinated  $\text{M}(\text{CO})_5$  fragments.

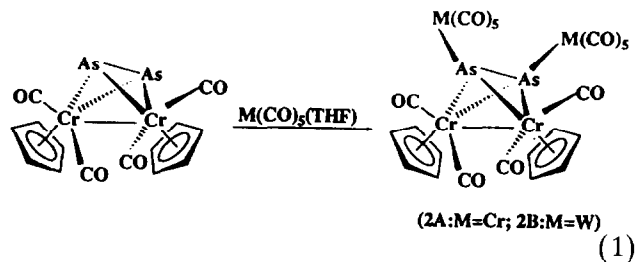
**Keywords:** Arsenic; Chromium; Tungsten; Carbonyl; Adduct; Cyclopentadienyl

## 1. Introduction

There is continuing interest in transition metal complexes containing bare main group elements. Those involving arsenic have been included in several recent reviews [1]. In our reaction of  $[\text{CpCr}(\text{CO})_3]_2$  with elemental arsenic, we have previously isolated  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (**1**) and  $\text{CpCr}(\text{CO})_2\text{As}_3$  as the primary products [2]. In the course of this study, we attempted an investigation into the donor capability of the coordinated  $\text{As}_2$  ligand towards the transition metal carbonyl fragments  $[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Cr}, \text{W}$ ), for purposes of comparison with the Mo analogue **3A** [3] of **2A** and its parent **3** [4], as well as with the ( $\mu\text{-}\eta^2\text{-P}_2$ ) analogue [5] of **2A**.

## 2. Results and discussion

The reaction of **1** with 2 mol equiv. of  $\text{M}(\text{CO})_5(\text{THF})$  [ $\text{M} = \text{Cr}, \text{W}$ ] at ambient temperature led to the isolation of the complexes  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{M}(\text{CO})_5]_2$  (**2A**,  $\text{M} = \text{Cr}$ , **2B**,  $\text{M} = \text{W}$ ) in 59.6 and 55.2% yields, respectively, as shown in Eq. 1.



The molecules are isostructural. A perspective view of **2A** is presented in Fig. 1. Selected bond parameters of the  $\text{Cr}_2\text{As}_2$  core of the molecules are compared with those of the parent compound **1** in Table 1. Table 2 gives significant bond parameters of **2A** compared with those of its Mo analogue (**3A**) and parent (**3**). The  $\text{Cr}_2\text{As}_2$  cores in these analogous molecules all possess a similar geometry, with the crystallographic  $C_2$  axis passing through the midpoints of the As–As and M–M bonds. The As–As' distances in **2A** and **2B** (2.284(2) Å), although lying between the observed range for such complexes, i.e. 2.273 Å in  $\text{Co}_2(\text{CO})_5(\text{PPh}_3)\text{As}_2$  [6] and 2.312(3) in **3**, is, contrary to expectation, slightly longer than in the parent  $\text{As}_2$  complex **1** (2.276(1) Å) [2]. The shortening of the As–As distance in these complexes, compared with that in gaseous  $\text{As}_4$  (2.44 Å) [7], has been ascribed to a partial charge transfer from the  $\text{As}_2$

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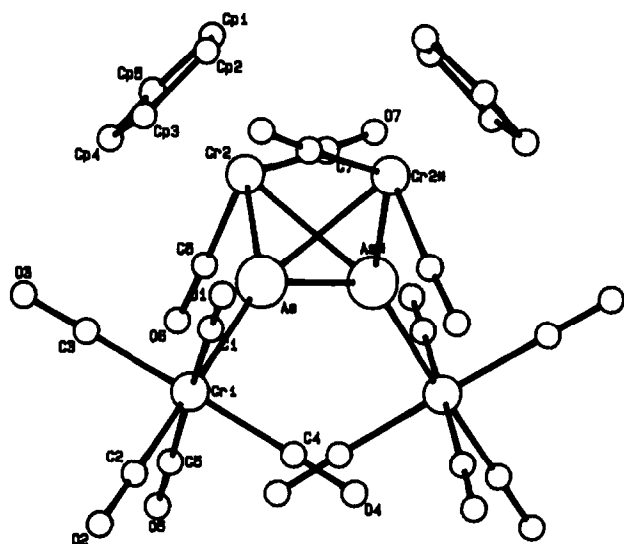


Fig. 1.

moiety to the metal fragment “electron sink”, thereby decreasing electron-pair repulsion between the As atoms [6]. In view of this, the coordination of the As<sub>2</sub> ligand to two electron-attracting M(CO)<sub>5</sub> groups would be expected to cause a further reduction in the As–As distance. However, this effect was not observed here, or for **3A** [3] or in the ( $\mu$ - $\eta^2$ -P<sub>2</sub>) analogue of **2A** [5].

Steric hindrance due to the two M(CO)<sub>5</sub> groups is obvious in all the adducts **2A**, **2B** and **3A**. Alleviation of this hindrance by increasing the dihedral angle MAsAs'M' is reflected in increases of the Mo/Cr2–Mo'/Cr2' distance and the Mo/Cr2–As–Mo'/Cr2' angle, accompanied by decreases in the As'–Mo/Cr2–Mo'/Cr2' and As–Mo/Cr2–Mo'/Cr2' angles (Tables 1 and 2). While both the Mo–As and Mo–As' distances are slightly shortened in **3A** (2.53 and 2.65 Å [3]) compared with those in the parent complex **3** (2.57 and 2.67 Å [5], respectively), in the case of **1** the Cr–As distances in its adducts are shortened (from 2.45 to 2.43 Å), whereas the Cr–As' distance are slightly lengthened (from 2.60 to 2.61 Å), making the AsAs'Cr triangle even more distorted. Likewise, as shown in Table 1, the Cr–CO distances have been increased from 1.86 to 1.87 Å and from 1.83 to 1.86 Å in **2A** and 1.85 Å in **2B**.

### 3. Experimental

All general procedures and spectral measurements were as described previously [5]. Complex **1** was synthesized from [CpCr(CO)<sub>3</sub>]<sub>2</sub> [2].

#### 3.1. X-ray structural analysis

Data collection and processing parameters for **2A** and **2B** are summarized in Table 3. The structures were

Table 1

Comparison of selected bond lengths (Å) and angles (°) of the Cr<sub>2</sub>As<sub>2</sub> core of **2A** and **2B** with those of **1**

	<b>1</b>	<b>2A</b>	<b>2B</b>
As–As'	2.276(1)	2.284(1)	2.285(2)
Cr–Cr'	3.026(1)	3.070(2)	3.071(3)
As–Cr'	2.597(1)	2.610(1)	2.606(2)
As–Cr	2.452(1)	2.431(1)	2.426(2)
Cr–C6	1.859(6)	1.871(8)	1.87(1)
Cr–C7	1.829(7)	1.859(7)	1.85(1)
As'–As–Cr	60.0(1)	59.14(3)	59.03(4)
As'–As–Cr'	66.5(1)	67.13(3)	67.12(4)
Cr'–As–Cr	73.6(1)	74.94(5)	75.13(6)
As–Cr–As'	53.5(1)	53.73(3)	53.86(5)
Cr'–Cr–As'	51.0(1)	49.88(3)	49.76(4)
As'–Cr–C7	71.8(2)	71.4(2)	71.5(4)
As'–Cr–C6	79.4(2)	81.3(2)	81.4(4)
Cr'–Cr–As	55.4(1)	55.17(3)	55.11(4)
As–Cr–C7	125.2(2)	125.0(2)	125.3(4)
As–Cr–C6	85.6(2)	86.8(2)	85.9(4)
Cr'–Cr–C7	89.3(2)	87.9(2)	88.8(4)
Cr'–Cr–C6	128.3(2)	129.1(2)	128.8(4)
C6–Cr–C7	87.8(3)	89.2(3)	89.2(5)

solved by the direct method MULTAN [8]. Non-hydrogen atoms were refined anisotropically by full matrix least-squares refinement. H atoms were located from the difference Fourier map and were refined isotropically. All computations were performed on a micro VAX II minicomputer using the MolEN package [9]. Residual electron densities were observed near the W atoms in **2B**. Atomic coordinates and their equivalent isotropic thermal parameters are given in Tables 4 and 5. Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

Table 2

Some selected bond lengths (Å) and angles (°) of [Cp(CO)<sub>2</sub>M]<sub>2</sub>As<sub>2</sub> [Cr(CO)<sub>5</sub>]<sub>2</sub> (**2A**, M = Cr; **3A**, M = Mo) and [Cp(CO)<sub>2</sub>Mo]<sub>2</sub>As<sub>2</sub> (**3**)

	<b>2A</b>	<b>3A</b> [3]	<b>3</b> <sup>a</sup> [4]
As–As'	2.284(1)	2.310(3)	2.312(3)
Cr1–As	2.479(1)	2.471(3)	
Mo/Cr2–Mo'/Cr2'	3.070(2)	3.064(3)	3.038(2)
Mo/Cr2–As	2.431(1)	2.531(3)	2.568(2)
Mo/Cr2–As'	2.610(1)	2.645(3)	2.670(2)
Mo/Cr2–CO	1.859–1.871(8)	1.96–1.98(1)	
Mo/Cr2–Cp	2.158–2.243(8)	2.28–2.237(1)	
Cr1–CO <sub>ax</sub>	1.846(8)	1.81(1)	
Cr1–CO <sub>eq</sub>	1.888–1.895(9)	1.84–1.88(1)	
Mo/Cr2–As'–As	67.13(3)	66.1(1)	66.1(1)
Mo/Cr2–As–As'	59.14(3)	–	61.6(1)
Mo/Cr2–As–Mo'/Cr2'	74.94(5)		70.9(1)
As–Mo/Cr2–As'	53.73(3)	53.0(1)	52.3(1)
As–Mo/Cr2–Mo'/Cr2'	55.17(3)	55.5(1)	56.2(0)
As'–Mo/Cr2–Mo'/Cr2'	49.88(3)		53.0(0)
Cr1–As–Mo/Cr2	146.75(4)	147.2(1)	
Cr1–As–As'	135.57(3)	135.4(1)	

<sup>a</sup> Average for two crystallographically independent molecules.

### 3.2. Preparation of $M(\text{CO})_5(\text{THF})$ solutions

Solutions of  $M(\text{CO})_5(\text{THF})$  ( $M = \text{Cr}, \text{W}$ ) (0.007 M) were prepared from  $M(\text{CO})_6$  in THF as described by Strohmeier and co-workers [10].

### 3.3. Isolation of $[\text{CpCr}(\text{CO})_2]_2\text{As}_2[\text{Cr}(\text{CO})_5]_2$ (**2A**)

An orange–yellow solution of  $\text{Cr}(\text{CO})_5(\text{THF})$  (41 ml, 0.29 mmol) was injected into a deep-purple solution of  $[\text{CpCr}(\text{CO})_2]_2\text{As}_2$  (70 mg, 0.14 mmol) in THF (5 ml) and the mixture was stirred at ambient temperature. After 1 h, the reaction mixture had turned purplish brown. After 3 h, the product mixture was evacuated to

dryness and the residue was dissolved in toluene (ca. 2 ml). Chromatography on a silica gel column (1.5 cm  $\times$  15 cm) prepared in *n*-hexane gave two fractions: (i) a yellow solution in *n*-hexane (10 ml) which, when concentrated to dryness, yielded an uncharacterized yellowish brown non-Cp-containing oily residue (12 mg), probably derived from unreacted  $\text{Cr}(\text{CO})_5\text{THF}$ ; (ii) a purplish brown solution in toluene (20 ml) followed by 1 : 1 toluene–diethylether (20 ml), which on concentration to ca. 2.5 ml and crystallization at  $-28^\circ\text{C}$  overnight gave a fine, dark, crystalline solid of **2A** (53 mg, 0.060 mmol, 42.7% yield) followed by a second crop (21 mg, 0.024 mmol, 16.9% yield). Anal. Found: C, 32.75; H, 0.92, As, 16.70; Cr, 23.15.  $\text{C}_{24}\text{H}_{10}\text{O}_{14}\text{As}_2\text{Cr}_4$  Calc.: C,

Table 3  
Data collection and processing parameters

Parameter	<b>2A</b>		<b>2B</b>	
Molecular formula	$\text{C}_{24}\text{H}_{10}\text{O}_{14}\text{As}_2\text{Cr}_4$		$\text{C}_{24}\text{H}_{10}\text{O}_{14}\text{As}_2\text{Cr}_2\text{W}_2$	
$M_r$	880.17		1143.88	
Crystal colour and habit	Black trigonal prism		Black trigonal prism	
Crystal size (mm)	0.14 $\times$ 0.18 $\times$ 0.22		0.1 $\times$ 0.2 $\times$ 0.3	
Unit cell parameters:				
$a$ (Å) $\alpha$ (°)	18.590(2)	90	18.7689(7)	90
$b$ (Å) $\beta$ (°)	10.4405(4)	110.088(7)	10.6810(8)	109.726(4)
$c$ (Å) $\gamma$ (°)	16.633(2)	90	16.6130(8)	90
$V$ (Å <sup>3</sup> ) $Z$	3031.9(8)	4	3135.0(5)	4
$D_x$ (mg m <sup>-3</sup> )	1.928		2.423	
Crystal system	Monoclinic		Monoclinic	
Space group	$C2/c$		$C2/c$	
Radiation	Mo K $\alpha$		Mo K $\alpha$	
No. of reflections for lattice parameters	25		25	
$\theta$ range for lattice parameters (°)	12–14		13–14.5	
Absorption coefficient (cm <sup>-1</sup> )	35.89		102.9	
Temperature (K)	299		300	
Diffractometer type	CAD4		CAD4	
Collection method	$\omega - 2\theta$		$\omega - 2\theta$	
Absorption correction type	$\psi$ -Scan		$\psi$ -Scan	
Absorption correction ( $T_{\min}$ , $T_{\max}$ )	82.167, 99.867		58.078, 99.825	
No. of reflections measured	5842		3016	
No. of independent reflections	2669		2752	
$\theta_{\max}$ (°)	25		25	
No. of observed reflections	1628		1872	
No. of standard reflections (and interval)	3(400)		3(400)	
Criterion for observed	$> 3\sigma(I)$		$> 3\sigma(I)$	
Variation of standards (% h <sup>-1</sup> )	$2.07 \times 10^{-2}$		$-9.79 \times 10^{-2}$	
$h_{\min}$ $h_{\max}$	0	22	-22	0
$k_{\min}$ $k_{\max}$	0	12	0	12
$l_{\min}$ $l_{\max}$	-19	18	-18	19
$R$	0.035		0.030	
$wR$	0.038		0.033	
No. of parameters refined	219		219	
No. of reflections used in refinement	1628		1872	
$S$	1.06		1.015	
Weighting scheme: $w =$	$1/\sigma(F)^2$		$1/\sigma(F)^2$	
$(\Delta/\sigma)_{\max}$	0.01		0.11	
$(\Delta\rho)_{\max}$ (e Å <sup>-3</sup> )	0.385		0.945	

32.73; H, 1.14; As, 17.05; Cr, 23.64%. NMR ( $C_6D_6$ ):  $^1H$   $\delta(Cp)$  4.03;  $^{13}C$   $\delta(Cp)$  87.28. IR (Nujol):  $\nu(CO)$  2071s, 2059s, 1979vs, 1945vs, 1920vs,  $\nu(others)$  1061vw, 873vw, 842w, 723w, 660s, 647s, 594w, 554s, 531w, 479vw, 450vw  $cm^{-1}$ .

### 3.4. Isolation of $[CpCr(CO)_2]_2As_2[W(CO)_5]_2$ (**2B**)

The procedure as described above was repeated for a mixture of  $[CpCr(CO)_2]_2As_2$  (70 mg, 0.14 mmol) in THF (5 ml) and  $W(CO)_5(THF)$  (41 ml, 0.29 mmol). Similar chromatography of the resultant purplish brown product mixture gave two fractions: (i) a yellow solution in *n*-hexane (12 ml) which, when concentrated to dryness, yielded an uncharacterized non-Cp-containing oily brown residue (13 mg), probably derived from  $W(CO)_5(THF)$ ; (ii) a brown solution in toluene (25 ml) followed by 1:1 toluene–diethylether (20 ml), which was concentrated to ca. 2.5 ml and allowed to crystallize at  $-28^\circ C$  overnight, yielding a fine, dark, crystalline solid of **2B** (66 mg, 0.058 mmol, 40.9% yield), followed by a second crop (23 mg, 0.020 mmol, 14.3% yield). Anal. Found: C, 25.69; H, 1.05; As, 12.93; Cr,

Table 4

Atomic coordinates and equivalent isotropic temperature factors for  $[CpCr(CO)_2]_2As_2[Cr(CO)_5]_2$ <sup>a</sup>

Atom	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
As	0.43843(3)	0.10112(6)	0.20323(4)	2.23(1)
Cr1	0.33550(5)	-0.0610(1)	0.14970(6)	2.95(2)
Cr2	0.51876(5)	0.25854(9)	0.16704(5)	2.45(2)
O1	0.2211(3)	0.0811(6)	0.2091(5)	9.9(2)
O2	0.2118(3)	-0.2572(6)	0.0797(3)	7.3(2)
O3	0.2824(4)	0.0794(7)	-0.0204(4)	8.2(2)
O4	0.3895(4)	-0.2086(6)	0.3167(4)	8.3(2)
O5	0.4406(3)	-0.2291(6)	0.0915(4)	7.2(2)
O6	0.5738(3)	0.0434(5)	0.0821(3)	5.3(1)
O7	0.6820(3)	0.3227(5)	0.2710(3)	5.1(1)
Cp1	0.5190(4)	0.4610(6)	0.1298(4)	4.2(2)
C1	0.2649(4)	0.0314(7)	0.1869(5)	5.4(2)
Cp2	0.4487(4)	0.4386(7)	0.1397(4)	4.4(2)
C2	0.2595(4)	-0.1817(8)	0.1060(4)	4.4(2)
Cp3	0.4100(4)	0.3442(7)	0.0810(4)	4.4(2)
C3	0.3024(4)	0.0264(8)	0.0438(5)	4.9(2)
C4	0.3690(4)	-0.1512(7)	0.2544(5)	4.4(2)
Cp4	0.4570(4)	0.3092(7)	0.0341(4)	4.4(2)
C5	0.4025(4)	-0.1640(7)	0.1133(4)	4.1(2)
Cp5	0.5248(4)	0.3799(7)	0.0645(4)	4.1(2)
C6	0.5537(3)	0.1239(6)	0.1158(4)	3.3(1)
C7	0.6197(3)	0.2952(6)	0.2331(4)	3.1(1)
H1	0.559(2)	0.516(4)	0.163(3)	1(1) *
H2	0.433(3)	0.479(5)	0.183(3)	3(1) *
H3	0.361(3)	0.307(5)	0.073(3)	3(1) *
H4	0.442(3)	0.248(5)	-0.010(3)	4(1) *
H5	0.561(4)	0.368(6)	0.046(4)	6(2) *

<sup>a</sup> Atoms with asterisks were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

Table 5

Atomic coordinates and equivalent isotropic temperature factors for  $[CpCr(CO)_2]_2As_2[W(CO)_5]_2$ <sup>a</sup>

Atom	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
W	0.33372(2)	-0.05671(4)	0.14990(2)	2.898(7)
As	0.43918(4)	0.11182(8)	0.20348(5)	2.37(2)
Cr'	0.48136(7)	0.2650(1)	0.33318(7)	2.50(3)
O1	0.2134(4)	0.0886(9)	0.2099(7)	10.7(3)
O2	0.2075(4)	-0.2572(9)	0.0787(5)	7.7(2)
O3	0.2824(5)	0.082(1)	-0.0300(5)	9.4(3)
O4	0.3863(6)	-0.1978(9)	0.3270(5)	8.9(3)
O5	0.4444(5)	-0.233(1)	0.0945(6)	8.7(3)
O6'	0.4293(4)	0.0547(7)	0.4198(4)	5.2(2)
O7'	0.3188(3)	0.3232(8)	0.2314(4)	5.3(2)
C1	0.2586(5)	0.038(1)	0.1879(8)	6.0(3)
C2	0.2548(5)	-0.184(1)	0.1059(6)	4.7(2)
C3	0.3006(5)	0.030(1)	0.0341(7)	5.0(3)
C4	0.3684(5)	-0.143(1)	0.2641(6)	4.9(3)
C5	0.4056(5)	-0.167(1)	0.1140(7)	5.0(3)
C6'	0.4487(5)	0.1318(9)	0.3854(5)	3.4(2)
C7'	0.3815(5)	0.2986(9)	0.2694(5)	3.3(2)
Cp1'	0.4819(6)	0.4628(9)	0.3695(6)	4.5(2)
Cp2'	0.5510(5)	0.439(1)	0.3601(6)	4.5(2)
Cp3'	0.5894(5)	0.349(1)	0.4179(6)	4.5(2)
Cp4'	0.5431(6)	0.315(1)	0.4660(6)	4.9(3)
Cp5'	0.4758(5)	0.383(1)	0.4362(6)	4.7(2)
H1'	0.441(4)	0.509(8)	0.333(5)	4(2) *
H2'	0.567(4)	0.469(8)	0.319(5)	5(2) *
H3'	0.634(5)	0.309(9)	0.432(5)	6(3) *
H4'	0.560(3)	0.262(7)	0.508(4)	2(2) *
H5'	0.431(5)	0.39(1)	0.451(5)	6(2) *

<sup>a</sup> Atoms with asterisks were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

9.35; W, 31.72.  $C_{24}H_{10}O_{14}As_2Cr_2W_2$  Calc.: C, 25.17; H, 0.87; As, 13.11; Cr, 9.09; W, 32.17%. NMR ( $C_6D_6$ ):  $^1H$   $\delta(Cp)$  4.01 and  $^{13}C$   $\delta(Cp)$  87.46. IR (Nujol):  $\nu(CO)$  2077s, 2066s, 1980vs, 1941vs, 1907vs,  $\nu(others)$  873vw, 843w, 821 vw, 723w, 589s, 573s, 554s, 532w, 480w  $cm^{-1}$ .

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