Journal of Organometallic Chemistry, 373 (1989) 71–76
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20014

Linkage of a pentacarbonylchromium fragment to a (μ-η^2-P_2)Cr_2 core. Crystal structure of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)[Cr(CO_5)]$

Lai Yoong Goh *, **Richard C.S. Wong,**

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

and

Thomas C.W. Mak *

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

(Received March 22nd, 1989)

Abstract

The complex $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)[Cr(CO)_5]$ (**2**) formed in the reaction of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)$ (**1**) with one molar proportion of $Cr(CO)_5(THF)$, has been structurally characterized. Crystal data: triclinic, space group $P\bar{1}$, a 7.859(4), b 9.948(5), c 16.209(8) Å, α 104.29(3), β 97.30(3), γ 108.90(3)°, and $Z = 2$. The molecular geometry of **2** is compared with those of **1** and $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)[Cr(CO)_5]_2$ (**3**).

Introduction

There is much current interest in the chemistry of transition metal complexes incorporating P_1 to P_4 units as ligands [1–3]. We have recently described [4] the synthesis of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)$ (**1**) from the reaction of $Cp_2Cr_2(CO)_6$ with P_4, and in a study of its reactions the linkage of one or two $M(CO)_5$ fragments ($M = Cr$, Mo, W) to the (μ-η^2-P_2)Cr_2 core was observed [5]. We describe here the crystal structure of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)[Cr(CO)_5]$ (**2**).

Experimental

Preparation of $Cp_2Cr_2(CO)_4(\mu$-η^2-$P_2)[Cr(CO)_5]$ (2)

Compound **2** was prepared as previously described [5], and recrystallised from toluene layered with n-hexane at ambient temperature. Dark reddish brown chunky rectangular plates suitable for an X-ray diffraction study were obtained after 3 days.

0022-328X/89/$03.50

Table 1

Data collection and processing parameters of compound (**2**)

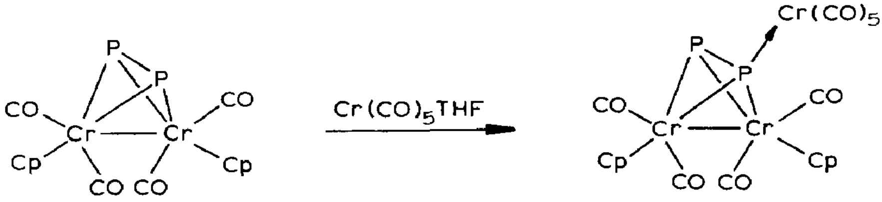
Molecular formula	$C_{19}H_{10}O_9P_2Cr_3$	
Molecular weight	600.22	
Unit cell parameters	a 7.859(4) Å	α 104.29(3)°
	b 9.948(5) Å	β 97.30(3)°
	c 16.209(8) Å	γ 108.90(3)°
	V 1132(1) Å^3	$Z = 2$
Density (calcd)	1.761 g cm^{-3}	
Space group	$P\bar{1}$	
Radiation	graphite-monochromatized Mo-K_α, λ 0.71073 Å	
Absorption coefficient	15.67 cm^{-1}	
Crystal size	0.40 × 0.38 × 0.36 mm	
Mean μr	0.295	
Transmission factors	0.502–0.814	
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}	
Scan range	0.65° below K_{α_1} to 0.65° above K_{α_2}	
Background counting	stationary counts for one-half of scan time at each end of scan range	
Collection range	h, $\pm k$, $\pm l$; $2\theta_{max}$ 55°	
Unique data measured	5234	
Observed data with $\|F_o\| > 4\sigma(\|F_o\|)$, n	4094	
Number of variables, p	298	
$R_F = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.077	
Weighting scheme	$w = [\sigma^2(F_o) + 0.001\|F_o\|^2]^{-1}$	
$R_G = [\Sigma_w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.092	
$S = [\Sigma_w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	2.030	
Residual extrema in final difference map	+1.21 to −1.16 eÅ^{-3}	

X-Ray structural analysis

The procedures for data collection, structure solution and refinement have been described previously [5]. Data collection and processing parameters are summarised in Table 1. Atomic coordinates and thermal parameters are given in Table 2. Tables of observed and calculated structure factors, hydrogen atomic coordinates and thermal parameters, and anisotropic thermal parameters are available from the authors.

Results and discussion

The reaction of $Cp_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (**1**) with one molar equivalent of $Cr(CO)_5(THF)$ yielded complex (**2**) in 60% yield [5].



A perspective view of molecule **2** is presented in Fig. 1. Selected bond lengths and bond angles are listed in Table 3. The measured Cr–Cr distance of 2.996(1) Å,

Table 2

Atomic coordinates ($\times 10^5$ for Cr and P; $\times 10^4$ for C and O atoms) and Thermal Parameters [a] (Å$^2 \times 10^4$ for Cr and P; $\times 10^3$ for C and O atoms) of **2**

Atom	x	y	z	U_{eq}
Cr(1)	10821(12)	39354(10)	29292(6)	327(3)
Cr(2)	22082(12)	39941(10)	12364(6)	349(4)
Cr(3)	44782(13)	86151(10)	31942(6)	393(4)
P(1)	26112(19)	60243(15)	25465(9)	315(5)
P(2)	57(19)	49199(17)	17615(9)	347(6)
C(1)	2630(10)	4320(8)	4242(4)	54(3)
C(2)	1134(11)	2955(9)	3986(5)	60(3)
C(3)	1400(10)	1997(8)	3264(5)	59(3)
C(4)	3048(10)	2764(8)	3066(5)	51(3)
C(5)	3815(9)	4202(8)	3674(4)	50(3)
C(6)	−137(9)	5018(8)	3547(4)	47(3)
O(1)	−903(8)	5628(7)	3951(3)	73(3)
C(7)	−1238(9)	2587(8)	2296(4)	48(3)
O(2)	−2692(7)	1728(6)	1954(4)	72(2)
C(8)	823(11)	2719(8)	−133(4)	57(3)
C(9)	−227(10)	2057(7)	378(4)	52(3)
C(10)	821(11)	1509(7)	890(5)	56(3)
C(11)	2526(12)	1849(8)	697(6)	67(4)
C(12)	2587(13)	2615(9)	74(5)	72(4)
C(13)	2870(9)	5585(8)	785(4)	47(3)
O(3)	3256(8)	6539(7)	482(4)	73(3)
C(14)	4624(9)	4624(8)	1841(5)	49(3)
O(4)	6131(7)	4985(7)	2192(4)	77(3)
C(15)	3318(11)	9057(7)	2262(5)	60(3)
O(5)	2623(11)	9347(7)	1714(4)	102(4)
C(16)	6354(11)	8486(8)	2588(5)	60(3)
O(6)	7501(9)	8461(8)	2229(5)	98(4)
C(17)	5790(10)	10650(8)	3736(5)	54(3)
O(7)	6557(8)	11886(5)	4065(4)	74(3)
C(18)	5670(10)	8147(7)	4121(5)	56(3)
O(8)	6402(10)	7875(7)	4663(4)	99(3)
C(19)	2551(12)	8751(8)	3763(5)	63(3)
O(9)	1399(10)	8889(8)	4088(6)	106(4)

[a] Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised U matrix.

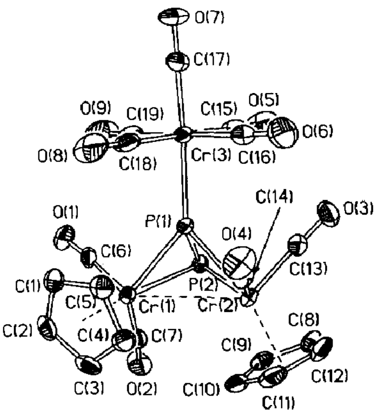


Fig. 1. Perspective view of $Cp_2Cr(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]$ (**2**).

Table 3

Bond lengths (Å) and selected bond angles (deg) for **2**

Cr(1)–Cr(2)	2.996(1)		
Cr(1)–P(1)	2.314(2)	Cr(1)–P(2)	2.510(2)
Cr(1)–C(1)	2.190(7)	Cr(1)–C(2)	2.172(9)
Cr(1)–C(3)	2.207(9)	Cr(1)–C(4)	2.236(9)
Cr(1)–C(5)	2.226(8)	Cr(1)–C(6)	1.860(8)
Cr(1)–C(7)	1.854(6)	Cr(2)–P(1)	2.447(2)
Cr(2)–P(2)	2.364(2)	Cr(2)–C(8)	2.196(6)
Cr(2)–C(9)	2.219(5)	Cr(2)–C(10)	2.243(7)
Cr(2)–C(11)	2.205(9)	Cr(2)–C(12)	2.156(9)
Cr(2)–C(13)	1.857(8)	Cr(2)–C(14)	1.847(7)
Cr(3)–P(1)	2.392(2)	Cr(3)–C(15)	1.882(9)
Cr(3)–C(16)	1.893(9)	Cr(3)–C(17)	1.864(6)
Cr(3)–C(18)	1.903(8)	Cr(3)–C(19)	1.894(10)
P(1)–P(2)	2.052(2)	C(1)–C(2)	1.400(9)
C(1)–C(5)	1.402(11)	C(2)–C(3)	1.401(11)
C(3)–C(4)	1.396(11)	C(4)–C(5)	1.405(9)
C(6)–O(1)	1.140(10)	C(7)–O(2)	1.147(7)
C(8)–C(9)	1.375(11)	C(8)–C(12)	1.427(14)
C(9)–C(10)	1.417(12)	C(10)–C(11)	1.369(13)
C(11)–C(12)	1.403(14)	C(13)–O(3)	1.146(11)
C(14)–O(4)	1.143(8)	C(15)–O(5)	1.129(12)
C(16)–O(6)	1.137(12)	C(17)–O(7)	1.129(8)
C(18)–O(8)	1.125(11)	C(19)–O(9)	1.132(13)
Cr(1)–Cr(2)–P(1)	49.1(1)	Cr(1)–Cr(2)–P(2)	54.3(1)
Cr(2)–Cr(1)–P(1)	53.0(1)	Cr(2)–Cr(1)–P(2)	49.9(1)
Cr(1)–Cr(2)–C(13)	128.2(2)	Cr(1)–Cr(2)–C(14)	87.7(2)
Cr(2)–Cr(1)–C(6)	129.6(2)	Cr(2)–Cr(1)–C(7)	88.7(2)
P(1)–Cr(1)–P(2)	50.1(1)	P(1)–Cr(1)–C(6)	88.5(2)
P(2)–Cr(1)–C(6)	81.3(2)	P(1)–Cr(1)–C(7)	121.8(3)
P(2)–Cr(1)–C(7)	71.8(3)	C(6)–Cr(1)–C(7)	86.6(3)
P(1)–Cr(2)–P(2)	50.5(1)	P(1)–Cr(2)–C(13)	80.8(2)
P(2)–Cr(2)–C(13)	86.3(2)	P(1)–Cr(2)–C(14)	73.6(2)
P(2)–Cr(2)–C(14)	123.9(2)	C(13)–Cr(2)–C(14)	89.6(3)
P(1)–Cr(3)–C(15)	90.1(2)	P(1)–Cr(3)–C(16)	93.5(2)
C(15)–Cr(3)–C(16)	89.0(4)	P(1)–Cr(3)–C(17)	175.8(3)
C(15)–Cr(3)–C(17)	89.5(3)	C(16)–Cr(3)–C(17)	90.7(3)
P(1)–Cr(3)–C(18)	89.4(2)	C(15)–Cr(3)–C(18)	178.9(4)
C(16)–Cr(3)–C(18)	90.1(4)	C(17)–Cr(3)–C(18)	91.1(3)
P(1)–Cr(3)–C(19)	86.2(2)	C(15)–Cr(3)–C(19)	88.9(4)
C(16)–Cr(3)–C(19)	177.8(4)	C(17)–Cr(3)–C(19)	89.5(3)
C(18)–Cr(3)–C(19)	92.1(4)	Cr(1)–P(1)–Cr(2)	78.0(1)
Cr(1)–P(1)–Cr(3)	140.8(1)	Cr(2)–P(1)–Cr(3)	138.2(1)
Cr(1)–P(1)–P(2)	69.9(1)	Cr(2)–P(1)–P(2)	62.7(1)
Cr(3)–P(1)–P(2)	132.8(1)	Cr(1)–P(2)–Cr(2)	75.8(1)
Cr(1)–P(2)–P(1)	60.0(1)	Cr(2)–P(2)–P(1)	66.9(1)
C(2)–C(1)–C(5)	107.7(6)	C(1)–C(2)–C(3)	108.1(7)
C(2)–C(3)–C(4)	108.2(6)	C(3)–C(4)–C(5)	107.7(7)
C(1)–C(5)–C(4)	108.2(6)	Cr(1)–C(6)–O(1)	176.3(7)
Cr(1)–C(7)–O(2)	175.5(7)	C(9)–C(8)–C(12)	106.7(8)
C(8)–C(9)–C(10)	109.3(7)	C(9)–C(10)–C(11)	107.5(7)
C(10)–C(11)–C(12)	108.8(9)	C(8)–C(12)–C(11)	107.6(8)
Cr(2)–C(13)–O(3)	178.0(5)	Cr(2)–C(14)–O(4)	177.7(6)
Cr(3)–C(15)–O(5)	178.6(7)	Cr(3)–C(16)–O(6)	177.6(7)
Cr(3)–C(17)–O(7)	178.8(8)	Cr(3)–C(18)–O(8)	178.8(8)
Cr(3)–C(19)–O(9)	176.7(8)		

Table 4

A comparison of selected bond lengths and bond angles in **2**, its parent compound **1** and the $[Cr(CO)_5]_2$ adduct **3**

	$Cp_2Cr_2(CO)_4P_2$ (**1**) [4]	$Cp_2Cr_2(CO)_4P_2[Cr(CO)_5]$ (**2**) [a]	$Cp_2Cr_2(CO)_4P_2[Cr(CO)_5]_2$ (**3**) [5]
Cr(1)–Cr(2)	3.011(1)	2.996(1)	3.003(1)
P(1)–P(2)	2.060(1)	2.052(2)	2.063(1)
Cr(1)–P(1)	2.341(1)	2.314(2)	2.340(1)
Cr(1)–P(2)	2.474(1)	2.510(2)	2.489(1)
Cr(2)–P(1)	2.468(1)	2.447(2)	2.489(1)
Cr(2)–P(2)	2.353(1)	2.364(2)	2.340(1)
Cr(3)–P(1)	–	2.392(2)	2.397(1)
Cr(1)–P(1)–P(2)	68.1(1)	69.9(1)	68.5(1)
Cr(2)–P(1)–P(2)	61.9(1)	62.7(1)	61.0(1)
Cr(1)–P(2)–P(1)	61.4(1)	60.0(1)	61.0(1)
Cr(2)–P(2)–P(1)	67.6(1)	66.9(1)	68.5(1)
Cr(1)–P(1)–Cr(2)	77.5(1)	78.0(1)	76.9(1)
Cr(1)–P(2)–Cr(2)	77.2(1)	75.8(1)	76.9(1)
Cr(2)–Cr(1)–P(1)	53.1(1)	53.0(1)	53.8(1)
Cr(2)–Cr(1)–P(2)	49.6(1)	49.9(1)	49.3(1)
Cr(1)–Cr(2)–P(1)	49.4(1)	49.1(1)	49.3(1)
Cr(1)–Cr(2)–P(2)	53.2(1)	54.3(1)	53.8(1)
P(1)–Cr(1)–P(2)	50.6(1)	50.1(1)	50.5(1)
P(1)–Cr(2)–P(2)	50.5(1)	50.5(1)	50.5(1)
Cr(3)–P(1)–P(2)	–	132.8(1)	137.1(1)
Cr(1)–P(1)–Cr(3)	–	140.8(1)	142.5(1)
Cr(2)–P(1)–Cr(3)	–	138.2(1)	135.8(1)

[a] This work.

marginally different from those in **1** and **3**, is close to that predicted for a single bond [6]. The P–P bond distances are also very similar in all three complexes, falling within the range 2.019(9) to 2.154(4) Å observed for μ-η^2-P_2 complexes known to date [1]. Although on the whole there is very little difference in the dimensions of the central Cr(1)Cr(2)P(1)P(2) core unit of the complexes **1**–**3**, as shown in Table 4, there is closer agreement between those of the symmetrical molecules **1** and **3**, as expected. In the mono-coordinated species **2**, a slight contraction is observed in the bonding distances of P(1) (the P atom bonded to $Cr(CO)_5$) to P(2), Cr(1) and Cr(2) and a slight lengthening in the bonding distances of P(2) to Cr(1) and Cr(2), in agreement with slightly larger bond angles at P(1) and smaller bond angles at P(2). The significant difference between **2** and **3** lies in the much larger Cr(3)–P(1)–P(2) angle of **3**, which is consistent with the steric demands of two $Cr(CO)_5$ fragments coordinated to both atoms of the μ-η^2-P_2 ligands.

Complex **2** is the only mono-metallated derivative of a μ-η^2-P_2 complex to be structurally characterised. Similar mono-coordination has been observed in the analogous μ-η^2-As_2 ligand in $CpM_2(CO)_4As_2[Cr(CO)_5]$ (M = Mo, W) [7], which were characterised by elemental analysis, and in the unstable complex $Co_2(CO)_6As_2M(CO)_5$ (M = Cr, Mo, W) [8].

Acknowledgements

We thank the University of Malaya and the Ming Yu Cultural Foundation for financial support.

References

1 M. Di Varia, P. Stoppioni and M. Peruzzini, Polyhedron, 6 (1987) 351 (a review) and ref. therein.
2 O.J. Scherer, Angew. Chem., Int. Ed. Engl., 24 (1985) 924 (a review) and ref. therein.
3 M. Di Varia and L. Sacconi, Angew. Chem., Int. Ed. Engl., 21 (1982) 330 (a review) and ref. therein.
4 L.Y. Goh, R.C.S. Wong, C.K. Chu and T.W. Hambley, J. Chem. Soc., Dalton Trans., in press.
5 L.Y. Goh, R.C.S. Wong and T.C.W. Mak, J. Organomet. Chem., 364 (1989) 363.
6 R.D. Adams, D.E. Collins and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.
7 G. Huttner, B. Sigwarth, O. Scheidsteger, L. Zsolnai and O. Orama, Organometallics, 4 (1985) 326.
8 M. Müller and H. Vahrenkamp, J. Organomet. Chem., 253 (1983) 95.