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Synthesis, characterizations, and structures of group IV metal–chromium complexes bridged by the benzyloxide group

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Abstract

Bimetallic complexes, $(\eta^5\text{-}C_5H_5)_2MX[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ (M = Ti, X = Cl (**1**) or Br (**2**); M = Zr, X = $CH_2C_6H_5$ (**3**)), were prepared by reacting $(HOCH_2C_6H_5)Cr(CO)_3$ with the appropriate titanocene or zircocene alkyl. The complex, $(\eta^5\text{-}C_5H_5)_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ (**4**), was synthesized by reacting 2 molar equivalents of $(HOCH_2C_6H_5)Cr(CO)_3$ with $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$. These complexes have been characterized by elemental analysis, IR, ^1H, and ^{13}C NMR spectroscopy. The complex **2** crystallizes in the monoclinic space group $P2_1/a$ with $a = 7.892(1)$, $b = 21.167(2)$, $c = 11.345(3)$ Å, $\beta = 92.00(2)°$, $V = 1915.4(6)$ Å^3, and $Z = 4$. However, the complex **4** crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.984(2)$, $b = 11.349(4)$, $c = 16.074(4)$ Å, $\alpha = 96.14(3)°$, $\beta = 101.06(2)°$, $\gamma = 93.45(2)°$, $V = 1416.7(4)$ Å^3, and $Z = 2$. From the X-ray structures, IR, and NMR spectroscopy, the $(C_6H_5)Cr(CO)_3$ moiety seems unperturbed by the early metal center.

Introduction

In the search for new catalysts and for modeling of heterogeneous catalysis, the synthesis and study of metal cluster complexes has flourished. In the past two decades, a dramatic number of complexes have been prepared and numerous reviews [1–7] have appeared summarizing the results in this field. More recently, the synthesis and chemistry of complexes containing both early (group IV and V transition metals) and late (group VI and later transition metals) metal centers have attracted considerable attention [8]. One of the major reasons is that early–late heterobimetallic complexes offer the potentially cooperative features to activate small molecules, such as carbon monoxide.

One of the methods for the preparation of early–late heterobimetallic complexes is to employ difunctional ligands to bridge two metals in a complex [9]. These heterodifunctional ligands are usually phosphine-based ligands, such as OCH_2PPh_2, CH_2PPh_2, or $C_5H_4(CH_2)_nPPh_2$ [8]. However, the difunctional ligands used to bridge early–late metals without a phosphine donor end are found only in a few cases [10–12].

Here we report the synthesis, characterizations, and X-ray structures of group IV metal–chromium complexes bridged by a difunctional benzyloxide group

($OCH_2C_6H_5$). The general formulae of these complexes is $Cp_2MX[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ ($Cp = \eta^5\text{-}C_5H_5$; M = Ti, X = Cl or Br; M = Zr, X = $CH_2\text{-}C_6H_5$ or ($\mu\text{-}OCH_2C_6H_5)Cr(CO)_3$). In the complexes, the $(C_6H_5)Cr(CO)_3$ moiety seems unperturbed by the early transition metal center.

Experimental

Reagents and general techniques

The compounds $Cp_2Ti(CH_3)Cl$ [13], $Cp_2Ti(CH_3)Br$ [13], $Cp_2Zr(CH_3)_2$ [14], $Cp_2Zr(CH_2C_6H_5)_2$ [15], and $(HOCH_2C_6H_5)Cr(CO)_3$ [16] were prepared according to literature procedures. Solvents were dried by refluxing at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (benzene, hexane); all solvents were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry nitrogen atmosphere.

Preparation of $Cp_2TiCl[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ *(1)*

A mixture of $Cp_2Ti(CH_3)Cl$ (0.46 g, 2.01 mmol) and $(HOCH_2C_6H_5)Cr(CO)_3$ (0.49 g, 2.01 mmol) in 15 mL of benzene was stirred at room temperature under a nitrogen atmosphere for 3 h. The resulting red solution was filtered and pumped to dryness in vacuo to give an orange-red solid. The solid was dissolved in 10 mL of dichloromethane, and 15 mL of hexane was layered on to afford orange crystals (0.35 g, 38%), m.p. 143.8–146.5°C dec. Anal. Found: C, 52.56; H, 3.77%. $C_{20}H_{17}O_4ClCrTi$ calc.: C, 52.60; H, 3.75%. IR (Nujol mull): 1967m, 1882sh, 1867s, 1534vw, 1517vw, 1413w, 1343w, 1280w, 1262vw, 1221w, 1186w, 1102m, 1042w, 1020w, 1009w, 1002w, 912vw, 886vw, 852w, 843w, 833w, 807s, 793sh, 682m, 655m, 634sh, 624s, 612m, 592sh, 546m, 523m, 472m, 462m, 419w cm^{-1}.

Preparation of $Cp_2TiBr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ *(2)*

A mixture of $Cp_2Ti(CH_3)Br$ (0.306 g, 1.12 mmol) and $(HOCH_2C_6H_5)Cr(CO)_3$ (0.273 g, 1.12 mmol) in 10 mL of benzene was stirred at 5 ° C under a nitrogen atmosphere for 2 h. The resulting red solution was cooled at 5°C to afford red crystals (0.37 g, 65.9%), m.p. 149.1–150.7 ° C dec. Anal. Found: C, 47.75; H, 3.45%. $C_{20}H_{17}O_4BrCrTi$ calc.: C, 47.94; H, 3.42%. IR (Nujol mull): 1973m, 1872s, 1284w, 1191w, 1105m, 1046w, 1022w, 1006w, 890w, 855sh, 846w, 809m, 796sh, 720m, 687m, 671m, 626s, 615sh, 552w, 527m, 476sh, 464m cm^{-1}.

Preparation of $Cp_2Zr(CH_2C_6H_5)[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ *(3)*

A mixture of $Cp_2Zr(CH_2C_6H_5)_2$ (0.41 g, 1.02 mmol) and $(HOCH_2C_6H_5)\text{-}Cr(CO)_3$ (0.24 g, 0.98 mmol) in 20 mL of benzene was stirred at room temperature under a nitrogen atmosphere for 4 h. The resulting yellow solution was filtered and concentrated to about 5 mL. The concentrated solution was then cooled to 5°C to afford a greenish yellow solid (0.25 g, 45.9%), m.p. 138.4–141.2°C dec. Anal. Found: C, 58.56; H, 4.41%. $C_{27}H_{24}O_4CrZr$ calc.: C, 58.36; H, 4.35%. IR (Nujol mull): 1968s, 1890s, 1860s, 1591w, 1559vw, 1305vw, 1285vw, 1204w, 1192w, 1172vw, 1150vw, 1113m, 1041vw, 1014m, 984w, 911vw, 881w, 845w, 809sh, 802s, 749m, 731sh, 722sh, 702m, 680m, 665m, 630s, 615m, 543m, 531sh, 486m, 457m cm^{-1}.

Preparation of $Cp_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ *(4)*

A mixture of $Cp_2Zr(CH_3)_2$ (0.18 g, 0.72 mmol) and $(HOCH_2C_6H_5)Cr(CO)_3$ (0.35 g, 1.43 mmol) in 10 mL of benzene was stirred at 5°C under a nitrogen atmosphere for 2 h. The resulting pale green solution was filtered and pumped to dryness to give a greenish yellow solid. The solid was then dissolved in 15 mL of dichloromethane and 50 mL of hexane was added. The solution was cooled to −15°C to afford pale green crystals (0.16 g, 31.4%), m.p. 158.8–160.0°C dec. Anal. Found: C, 50.75, H, 3.49%. $C_{30}H_{24}O_8Cr_2Zr$ calc.: C, 50.91; H, 3.42%. IR (Nujol mull): 1970s, 1954s, 1909sh, 1896s, 1884s, 1850s, 1417w, 1350vw, 1290vw, 1199m, 1150m, 1103m, 1045vw, 1015w, 833w, 806s, 795sh, 726w, 708m, 665s, 637s, 620m, 610sh, 529s, 478m, 457w, 446m, 421w cm^{-1}.

Physical measurements

Infrared spectra were recorded on a Hitachi 270-30 spectrometer in the region of 4000–400 cm^{-1}; the peak positions were calibrated with the 1601.4 cm^{-1} peak of polystyrene. ^1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer and ^{13}C NMR spectra were recorded with the Varian VXR-300 (75.43 MHz) spectrometer. The proton chemical shifts were measured relative to TMS as the internal reference and ^{13}C chemical shifts were obtained using the deuteriated solvents as the internal reference. Melting points were measured under a nitrogen atmosphere using a Büchi 535 instrument and were not corrected. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument.

Crystal structure determinations

The size of the crystal of **2** for X-ray diffraction was 0.50 × 0.31 × 0.36 mm and the size of the crystal of **4** was 0.90 × 0.60 × 0.50 mm. Cell dimensions of **2** were obtained from 25 reflections with 2θ angle in the range of 15.46–33.94° and cell dimensions of **4** were obtained from 25 reflections with 2θ angle in the range of 15.14–32.80°. The diffraction intensities were collected on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-K_α radiation, λ = 0.70930 Å. All calculations were carried out using the NRCC package [17] on a VAX 780 computer. All atomic scattering factors were taken from the *International Tables for X-Ray Crystallography* [18]. The crystallographic data of complexes **2** and **4** are summarised in Table 1.

Results and discussion

Preparation of complexes

Dinuclear complexes, $Cp_2MX[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ (M = Ti, X = Cl (**1**) or Br (**2**); M = Zr, X = $CH_2C_6H_5$ (**3**)), were prepared by reaction of stoichiometric amounts of $(HOCH_2C_6H_5)Cr(CO)_3$ and the appropriate titanocene or zirconocene alkyls in benzene via the de-alkylation process (eq. 1).

$$Cp_2MRX + (HOCH_2C_6H_5)Cr(CO)_3 \rightarrow Cp_2MX[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3] + RH \qquad (1)$$

Table 1

Crystallographic data

Complex	$(\eta^5\text{-}C_5H_5)_2TiBr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ (**2**)	$(\eta^5\text{-}C_5H_5)_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ (**4**)
Formula	$C_{20}H_{17}BrO_4CrTi$	$C_{30}H_{24}O_8Cr_2Zr$
f_w	501.15	707.72
Crystal systems	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a (Å)	7.982(1)	7.984(2)
b (Å)	21.167(2)	11.349(4)
c (Å)	11.345(3)	16.074(4)
α (deg)		96.14(3)
β (deg)	92.00(2)	101.06(2)
γ (deg)		93.45(2)
V (Å^3)	1915.4(6)	1416.4(7)
Z	4	2
$D_{calc.}$ (g cm^{-3})	1.738	1.659
μ(Mo-K_α) (cm^{-1})	30.6	11.4
Minimum transmission factor	0.839	0.902
Scan mode	$\theta/2\theta$	$\theta/2\theta$
2θ(max) (deg)	44.9	44.9
No. of reflections measured	2715	4016
No. of unique reflections with $I > 2.5\sigma(I)$	1851	3328
No. of refined parameters	244	371
R_f [a] for significant reflections	0.031	0.028
R_w [b] for significant reflections	0.034	0.048
GoF [c]	1.67	1.35

[a] $R_f = [\Sigma|F_o - F_c|/\Sigma|F_o|]$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. [c] $GoF = [\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

In eq. 1, R is CH_3 for M = Ti and X = Cl or Br, and R = X = $CH_2C_6H_5$ for M = Zr. The trinuclear complex, $Cp_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ (**4**), was prepared in a similar way by reaction of 2 molar equivalents of $(HOCH_2C_6H_5)Cr(CO)_3$ and 1 molar equivalent of $Cp_2Zr(CH_3)_2$ in benzene. These complexes are soluble in dichloromethane, less soluble in benzene, and not soluble in diethyl ether or hexane. All complexes can be crystallized from benzene solution at 5°C or from dichloromethane/hexane solution. Complexes **1** and **2** are orange or orange-red crystals, respectively, and complexes **3** and **4** are pale green crystals. They are stable under a dry nitrogen atmosphere for at least several weeks.

In the preparation of $(HOCH_2C_6H_5)Cr(CO)_3$ and during the synthesis of the complexes, we found that $(HOCH_2C_6H_5)Cr(CO)_3$ decomposes gradually in the solid state and in solution to give a green insoluble material which, fortunately, can be removed by filtration after reactions.

Characterization of complexes

These complexes have been characterized by elemental analysis, infrared spectra, ^1H and ^{13}C NMR spectra. The infrared spectra of these complexes were obtained as the Nujol mull between KBr plates and some of the infrared bands

Table 2

Assignments of selected IR bands [a]

	1	**2**	**3**	**4**
ν(CO)	1967m 1882sh 1867s	1973m 1872s	1968s 1890s 1860s	1970s 1954s 1909sh 1896s 1884s 1850s
ν(C=C)	1534vw 1517vw		1591w 1559vw	
ν(C–O)	1102m	1105m	1113m	1103m

[a] As Nujol mulls between KBr plates. Additional frequencies are listed in the Experimental section. s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

(Table 2) are tentatively assigned. Three CO stretching bands are observed for **1** and **3**. For complex **2**, only two CO stretching bands are observed, however, the 1872 cm^{-1} band is somewhat broad and may contain two overlapping CO stretching bands. For complex **4**, six CO stretching bands indicate that two (η^6-C_6H_5)$Cr(CO)_3$ moieties in the complex are different. Very weak bands at 1500–1550 cm^{-1} observed for **1** are owing to ν(C=C) of the η^6-C_6H_5 group. The C–O stretching of these complexes is at ~ 1105 cm^{-1}, that is about 10–20 cm^{-1} lower than that of $Cp_2Zr(OR)X$ [19].

The ^1H and ^{13}C resonances are listed in Tables 3 and 4, respectively. It is found that the ^1H and ^{13}C chemical shifts of the (η^6-C_6H_5)$Cr(CO)_3$ moiety do not vary much for complexes **1–4**. However, the ^1H and ^{13}C chemical shifts of Cp and $-OCH_2-$ groups are affected more dramatically by the X group in the complex.

Table 3

^1H NMR data for complexes **1–4** [a]

Complex	C_5H_5	$-OCH_2-$	$-C_6H_5$	$-CH_2-$	C_6H_5
1	6.40 (s, 10H)	5.17 (s, 2H)	5.23 (m, 1H) 5.29 (m, 2H) 5.39 (m, 2H)		
2	6.43 (s, 10H)	5.13 (s, 2H)	5.23 (m, 1H) 5.27 (m, 2H) 5.39 (m, 2H)		
3	6.00 (s, 10H)	4.72 (s, 2H)	5.20-5.25 (m 3H) 5.45 (m, 2H)	2.32 (s, 2H)	6.79–6.82 (m, 3H) 7.14 (m, 2H)
4	6.31 (s, 10H)	4.83 (s, 4H)	5.21 (m, 2H) 5.32 (m, 4H) 5.43 (m, 4H)		

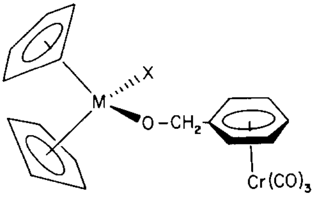
[a] Chemical shift is in ppm relative to 0 ppm of TMS in $CDCl_3$. s, singlet; m, multiplet.

Table 4

^{13}C NMR data for complexes **1-4** [a]

Complex	CO	C_5H_5	$-OCH_2-$	$-C_6H_5$	$-CH_2-$	C_6H_5
1	233.3	117.2	80.2	90.4 91.3 93.2		
2	233.3	116.9	80.6	90.4 91.4 93.2 113.8		
3	233.0	111.6	73.3	89.8 90.7 93.7 118.1	47.6	120.5 126.3 127.8 152.7
4	233.3	112.5	72.8	89.8 90.9 93.6 115.5		

[a] Chemical shift is in ppm relative to 77.0 ppm of $CDCl_3$ as solvent.



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The tendency of shift from downfield to upfield in ^1H NMR is in the order of $X = Cl \sim Br$, $(OCH_2C_6H_5)Cr(CO)_3$, and $CH_2C_6H_5$. This tendency reflects the shielding effect of these ligands [20]. The difference of chemical shifts for the Cp ring proton between complex **1** and **3** is 0.43 ppm and that for $-OCH_2-$ groups is 0.45 ppm. For ^{13}C NMR, a similar trend is observed.

Molecular structure of $Cp_2TiBr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ (2) and $Cp_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ (4)

Table 5 lists the final coordinates and isotropic thermal parameters for **2**. The Pluto drawing of **2** is shown in Fig. 1 and selected bond distances and bond angles are listed in Table 6. The average Ti–Cp carbon distance in **2** is 2.389(5) Å and the Ti–Cp centroid distances are 2.069 and 2.091 Å. The Cp ring centroid–Ti–Cp ring centroid angle is 132.93(4)°. These bond distances and bond angles seem normal compared with titanocene complexes [21–23]. The Ti–Br bond distance is 2.558(1) Å which is longer by ~ 0.1 Å than the Ti–Br bond distances in the less crowded complexes, $[(C_5Me_5)TiBr(\mu\text{-}O)]_4 \cdot CHCl_3$ [24] and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$ [25]. The Ti–O bond distance is 1.822(3) Å which is similar or somewhat longer than the Ti–O (bridging) bond distances in $[(C_5Me_5)TiBr(\mu\text{-}O)]_4 \cdot CHCl_3$ and $[(C_5Me_5)TiBr(\mu\text{-}O)]_3$. The Br–Ti–O angle is 93.11(11)°. The angle between the Cp ring centroid–Ti–Cp ring centroid plane and the Br–Ti–O plane is 92.35(6)°. The

Table 5

Final coordinates and isotropic thermal parameters for **2**

Atom	x	y	z	B_{iso}
Br	0.35914(8)	0.40702(3)	0.01384(5)	5.84(4)
Cr	0.17819(9)	0.64178(3)	−0.30636(6)	2.55(3)
Ti	0.29906(10)	0.39837(4)	−0.20849(7)	2.38(4)
O1	0.5474(5)	0.6454(2)	−0.3329(3)	5.29(21)
O2	0.1643(5)	0.5442(2)	−0.4973(3)	5.79(21)
O3	0.1478(6)	0.7400(2)	−0.4936(3)	6.58(22)
O4	0.1867(4)	0.4733(1)	−0.2171(3)	3.59(16)
C1	0.4078(7)	0.6441(2)	−0.3216(4)	3.12(22)
C2	0.1683(6)	0.5818(2)	−0.4237(4)	3.55(23)
C3	0.1590(6)	0.7020(2)	−0.4211(4)	3.78(24)
C4	0.0560(6)	0.5734(2)	−0.1881(4)	2.69(20)
C5	0.1968(6)	0.5982(2)	−0.1293(4)	2.87(21)
C6	0.2158(6)	0.6648(2)	−0.1181(4)	3.66(25)
C7	0.0942(7)	0.7049(2)	−0.1646(5)	4.02(25)
C8	−0.0477(6)	0.6799(2)	−0.2248(4)	3.81(24)
C9	−0.0671(6)	0.6149(2)	−0.2361(4)	3.42(23)
C10	0.0320(6)	0.5027(2)	−0.2021(4)	3.56(24)
C11	0.1498(7)	0.3252(3)	−0.3286(5)	4.21(26)
C12	0.0294(6)	0.3597(2)	−0.2706(5)	4.12(26)
C13	0.0457(7)	0.3475(3)	−0.1519(5)	4.63(28)
C14	0.1759(8)	0.3029(3)	−0.1365(5)	5.11(31)
C15	0.2406(7)	0.2894(2)	−0.2449(6)	4.68(32)
C16	0.4529(8)	0.4237(5)	−0.3762(5)	6.58(41)
C17	0.5167(8)	0.3665(3)	−0.3354(7)	5.90(35)
C18	0.5899(7)	0.3761(3)	−0.2268(6)	4.97(31)
C19	0.5806(7)	0.4391(4)	−0.2029(6)	5.40(33)
C20	0.5012(9)	0.4686(3)	−0.2933(8)	6.17(39)

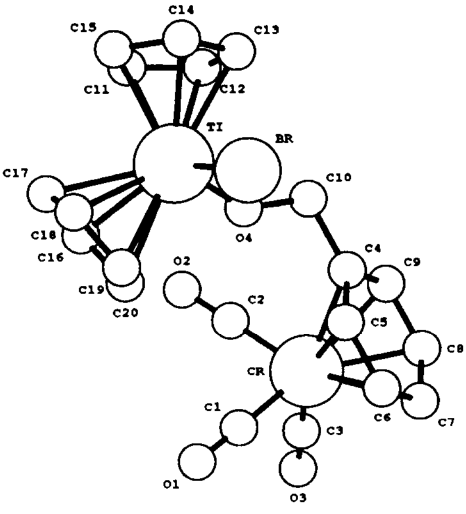

Fig. 1. Molecular structure of $Cp_2TiBr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]$ (**2**).

Table 6

Selected bond distances (Å) and bond angles (°) for **2**

Ti-Br	2.5576(11)	Ti-O4	1.822(3)
C4-C10	1.517(7)	C10-O4	1.398(6)
Cr-C1	1.847(5)	C1-O1	1.126(5)
Cr-C2	1.839(5)	C2-O2	1.153(7)
Cr-C3	1.824(5)	C3-O3	1.153(6)
Ti-Cp1	2.0688(8)	Ti-Cp2	2.0910(8)
Cr-Ph	1.7115(8)		
Cp1-Ti-Cp2	132.93(4)	Br-Ti-O	93.77(11)
Ti-O4-C10	144.7(3)	Cr-C1-O1	178.8(4)
Cr-C2-O2	179.1(5)	Cr-C3-O3	179.6(5)

Ti-O4-C10 angle is 144.7(3)°. For the $(C_6H_5)Cr(CO)_3$ moiety, the average Cr-phenyl carbon distance is 2.211(5) Å and the Cr-phenyl ring centroid distance is 1.711 Å. It is interesting that the phenyl ring plane is tilting down from the Br-Ti-O plane by an angle of 53.32°. The $(C_6H_5)Cr(CO)_3$ moiety is away from the bromine atom to avoid close contact and the titanium-chromium distance is 5.351(1) Å.

The final coordinates and isotropic thermal parameters of **4** are listed in Table 7. The molecular structure of **4** is shown in Fig. 2 and selected bond lengths and bond angles are listed in Table 8. The average Zr-Cp carbon distance in **4** is 2.532(4) Å and the Zr-Cp centroid distances are 2.249 and 2.251 Å. The distances of zirconium to two bonded oxygen atoms are 1.948(2) and 1.956(2) Å, respectively. These distances are similar to Zr-O(bridging) bond distances, but they are shorter by ~ 0.05 Å than the Zr-O bond distances in $Cp^*\overline{Zr(\mu\text{-}OCH_2PPh_2)_2Rh}Me_2$ [26]. The distances of the methylene carbon-oxygen bonds are 1.368(4) and 1.370(4) Å, which are about 0.03 Å shorter than in the titanium complex **2**. The longer

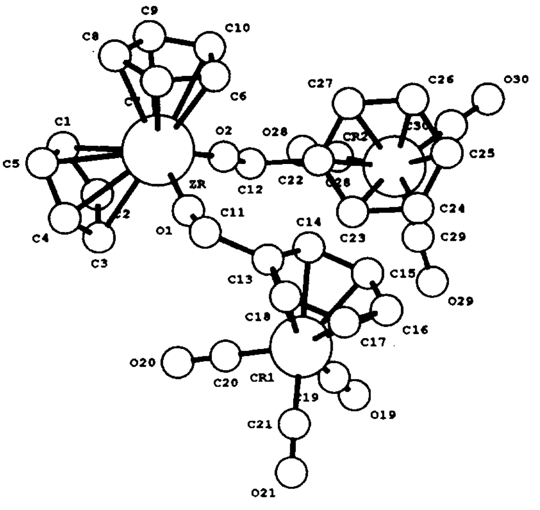

Fig. 2. Molecular structure of $Cp_2Zr[(\mu\text{-}OCH_2C_6H_5)Cr(CO)_3]_2$ (**4**).

Table 7

Final coordinates and isotropic thermal parameters for **4**

Atom	x	y	z	B_{iso}
Zr	0.81365(4)	0.08556(2)	0.20443(2)	2.56(2)
Cr1	1.26056(7)	0.24943(5)	0.51610(3)	3.01(2)
Cr2	1.28659(6)	0.53818(4)	0.14869(3)	2.69(2)
O1	0.8877(3)	0.1063(2)	0.3287(1)	4.4(1)
O2	0.9661(3)	0.2115(2)	0.1792(2)	5.5(1)
O19	1.5807(4)	0.3370(3)	0.4660(3)	7.6(2)
O20	1.2852(4)	0.0146(3)	0.4173(2)	6.4(2)
O21	1.4731(4)	0.1638(3)	0.6685(2)	6.8(2)
O28	1.3311(4)	0.3844(3)	−0.0073(2)	5.9(1)
O29	1.6648(3)	0.5562(3)	0.2075(2)	6.2(2)
O30	1.3140(5)	0.7520(3)	0.0574(2)	7.0(2)
C1	0.8357(8)	−0.0820(5)	0.0905(3)	7.0(3)
C2	1.0012(7)	−0.0403(4)	0.1247(3)	5.8(2)
C3	1.0379(5)	−0.0628(4)	0.2063(3)	5.4(2)
C4	0.8961(8)	−0.1207(4)	0.2236(4)	6.5(3)
C5	0.7720(6)	−0.1336(4)	0.1525(5)	7.6(3)
C6	0.5860(6)	0.2208(4)	0.2360(3)	5.9(2)
C7	0.5183(5)	0.1084(5)	0.2393(3)	5.9(3)
C8	0.4913(5)	0.0476(4)	0.1560(4)	6.5(3)
C9	0.5454(6)	0.1264(5)	0.1051(3)	5.8(2)
C10	0.5976(6)	0.2316(4)	0.1543(4)	6.0(2)
C11	0.8671(5)	0.1216(3)	0.4117(2)	3.9(2)
C12	1.0848(5)	0.2639(3)	0.1407(3)	4.9(2)
C13	0.9783(4)	0.2270(3)	0.4640(2)	3.1(1)
C14	1.0518(5)	0.3149(3)	0.4242(2)	3.8(2)
C15	1.1542(5)	0.4113(3)	0.4742(2)	4.1(2)
C16	1.1799(5)	0.4230(3)	0.5640(2)	3.9(2)
C17	1.1078(4)	0.3347(3)	0.6030(2)	3.7(2)
C18	1.0058(4)	0.2371(3)	0.5533(2)	3.4(1)
C19	1.4592(5)	0.3030(4)	0.4862(3)	4.6(2)
C20	1.2754(5)	0.1058(3)	0.4552(2)	4.1(2)
C21	1.3890(5)	0.1952(3)	0.6098(3)	4.5(2)
C22	1.1164(4)	0.3931(3)	0.1771(2)	3.7(2)
C23	1.2418(5)	0.4302(3)	0.2498(2)	4.1(2)
C24	1.2696(5)	0.5519(4)	0.2839(2)	4.4(2)
C25	1.1692(5)	0.6341(3)	0.2459(3)	4.7(2)
C26	1.0413(5)	0.5980(3)	0.1728(3)	4.4(2)
C27	1.0140(4)	0.4779(3)	0.1397(2)	3.9(2)
C28	1.3129(4)	0.4433(3)	0.0527(2)	3.8(2)
C29	1.5188(5)	0.5502(3)	0.1835(2)	3.7(2)
C30	1.3042(5)	0.6683(3)	0.0918(2)	4.2(2)

methylene carbon–oxygen bond in **2** may reflect the smaller size of the titanium atom which causes bigger steric hindrance. The Cp ring centroid–Zr–Cp ring centroid angle is 129.60(2)° and the O–Zr–O angle is 98.12(13)°. The angle between the Cp ring centroid–Zr–Cp ring centroid plane and the O–Zr–O plane is 89.78(8)°. The Zr–O–C angles at 155.94(22) and 157.9(3)° are substantially larger than the angle in complex **2** at 144.3°, in $Cp_2ZrMe[O-C(Me)=CPh_2]$ at 150.8°, and in $Cp_2Zr[O-C(Me)=CPh_2]_2$ at 144.2 and 143.5° [29]. The larger angles indicate steric crowding among Cp rings and two bulky $(C_6H_5)Cr(CO)_3$ groups. For

Table 8

Selected bond distances (Å) and bond angles (°) for **4**

Zr–O1	1.9561(23)	Zr–O2	1.9479(24)
O1–C11	1.370(4)	O2–C12	1.368(4)
C11–C13	1.516(5)	C12–C22	1.507(5)
Cr1–C19	1.831(4)	Cr2–C28	1.839(4)
Cr1–C20	1.832(4)	Cr2–C29	1.823(4)
Cr1–C21	1.838(4)	Cr2–C30	1.831(4)
C19–O19	1.140(5)	C28–O28	1.151(5)
C20–O20	1.159(5)	C29–O29	1.151(5)
C21–O21	1.151(5)	C30–O30	1.154(5)
Zr–Cp1	2.2485(8)	Zr–Cp2	2.2514(6)
Cr1–Ph1	1.7181(7)	Cr2–Ph2	1.7014(6)
Cp1–Zr–Cp2	129.600(24)	O1–Zr–O2	98.12(13)
Zr–O1–C11	155.94(22)	Zr–O2–C12	157.9(3)
Cr1–C19–O19	178.5(4)	Cr2–C28–O28	179.3(3)
Cr1–C20–O20	179.4(4)	Cr2–C29–O29	178.1(3)
Cr1–C21–O21	178.0(4)	Cr2–C30–O30	178.4(3)

$(C_6H_5)Cr(CO)_3$ moieties, the average Cr–phenyl carbon distance is 2.210(3) Å which is about the same as that in **2**. The distances of chromium to two phenyl ring centroids are 1.701 and 1.718 Å, respectively. One of the $(C_6H_5)Cr(CO)_3$ moieties is tilting away by an angle of 57.13(13)°. The angle between one phenyl ring and the O–Zr–O plane is nearly parallel at 169.16(13)° and the angle between another phenyl ring and the O–Zr–O plane is 119.53(13)°.

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