

The synthesis, characterizations and structures of Group 4 metal–chromium complexes bridged by an OC₆H₄CH₃ group

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Abstract

The bimetallic complexes, (η^5 -C₅H₅)₂MX[(OC₆H₄CH₃)Cr(CO)₃] (M = Ti; X = CH₃ (**1**), Cl (**2**) or Br(**3**)) (M = Zr; X = CH₂C₆H₅ (**5**)), were prepared by reaction of (η^5 -C₅H₅)₂MXR with 1 molar equivalent of (*p*-HOC₆H₄CH₃)Cr(CO)₃. The complexes, (η^5 -C₅H₅)₂M[(OC₆H₄CH₃)Cr(CO)₃]₂ (M = Ti (**4**) or Zr (**6**)), were prepared by reaction of (η^5 -C₅H₅)₂MR₂ with 2 molar equivalents of (*p*-HOC₆H₄CH₃)Cr(CO)₃. These complexes were characterized by the melting point, elemental analysis, and IR, ¹H and ¹³C NMR spectroscopy. Complex **3** crystallizes in the triclinic *P* $\bar{1}$ space group with cell parameters *a* = 7.682(2) Å, *b* = 10.262(3) Å, *c* = 13.838(4) Å, α = 109.43(2)°, β = 100.33(2)°, γ = 100.10(2)°, *R* = 0.072 and *R*_w = 0.090. Complex **4** crystallizes in the monoclinic *P*2₁/*c* space group with cell parameters *a* = 7.626(3) Å, *b* = 41.70(3) Å, *c* = 18.287(7) Å, β = 92.01(3)°, *R* = 0.050 and *R*_w = 0.062. Two independent molecules are found in a unit cell for **4**. Both **3** and **4** show unusually long Ti–O(aryl) bond distances which suggest severely steric crowdedness between titanocene and (arene)Cr(CO)₃ moieties. The conformations of Cr-carbonyl tripods are staggered relative to the oxygen donor for **3** and *syn*-eclipsed, *anti*-eclipsed and staggered for **4**.

Keywords: Chromium; Titanium; Zirconium

1. Introduction

The chemistry of (arene)Cr(CO)₃ has attracted extensive attention during the last two decades, and studies of these complexes have appeared in several reviews [1]. The main focuses of the studies are on the effect of donor–acceptor abilities of the substituent X of (X_nC₆H_{6–n})Cr(CO)₃ to the spectroscopic properties of the complexes [1a,2] and to the regioselectivities of the nucleophilic substitutions on the phenyl ring [1a,3]. Structurally, the non-planarity of the phenyl ring and the conformation of the Cr-carbonyl tripods can also be correlated with the donor–acceptor abilities of the ring substituents [4]. Recently, the ring-substituted arene chromium complexes (XC₆H₅)Cr(CO)₃ were used as metalloligands for the preparation of bimetallic complexes [5]. For these bimetallic complexes, it is interesting to see the effect of the second metal on the properties and on the structural variations of the (arene)Cr(CO)₃ moiety.

Here we report the synthesis of group 4 metal–chromium complexes bridged by an OC₆H₄CH₃ group which bears unequivalent *para*-disubstituted groups. The complexes prepared are Cp₂MX[(OC₆H₄CH₃)Cr(CO)₃] (Cp = η^5 -cyclopentadienyl) (M = Ti; X = CH₃ (**1**), Cl (**2**), Br (**3**) or (OC₆H₄CH₃)Cr(CO)₃ (**4**)) (M = Zr; X = CH₂C₆H₅ (**5**) or (OC₆H₄CH₃)Cr(CO)₃ (**6**)). The molecular structures of **3** and **4** were determined through X-ray analysis. The molecular structures of **3** and **4** show rather long Ti–O bond distances which may suggest severely steric crowdedness between titanocene and (arene)Cr(CO)₃ moieties. The conformation of Cr-carbonyl tripods are random owing to the steric crowdedness.

2. Experimental section

2.1. Reagents and general techniques

The compounds Cp₂Ti(CH₃)₂ [6], Cp₂Ti(CH₃)Cl [7], Cp₂Ti(CH₃)Br [7] and Cp₂Zr(CH₂C₆H₅)₂ [8] were prepared according to the literature procedures.

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$(\text{HO}C_6H_4CH_3)Cr(CO)_3$ [9] was prepared from reaction of $(CH_3CN)_3Cr(CO)_3$ [10] with *p*- $\text{HO}C_6H_4CH_3$ in refluxing tetrahydrofuran. *p*- $\text{HO}C_6H_4CH_3$ (Merck) was used without further purification. Solvents were dried by refluxing at least 24 h over P_2O_5 (dichloromethane) or sodium–benzophenone (*n*-hexane, diethyl ether, tetrahydrofuran and benzene) and were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

2.2. Synthesis of $Cp_2Ti(CH_3)[(OC_6H_4CH_3)Cr(CO)_3]$ (1)

To a solution of $Cp_2Ti(CH_3)_2$ (0.624 g, 3.0 mmol) in 30 ml of dichloromethane at -30°C , $(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.732 g, 3.0 mmol) was added slowly. The resulting mixture was stirred for 2 h and then was dried in vacuo to give a brown residue which was washed twice with 5 ml of diethyl ether each time to afford a yellowish-brown product (0.577 g (44.1%); melting point (m.p.), 159.7 – 160.9°C). Anal. Found: C, 57.53; H, 4.78. $C_{21}H_{20}O_4TiCr$ Calc.: C, 57.81; H, 4.62%. IR (Nujol): $\nu(\text{CO})$ 1946 (s), 1879 (sh), 1844 (s) cm^{-1} .

2.3. Synthesis of $Cp_2TiCl[(OC_6H_4CH_3)Cr(CO)_3]$ (2)

To a solution of $Cp_2Ti(CH_3)Cl$ (0.703 g, 3.1 mmol) in 35 ml of dichloromethane at 0°C , $(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.752 g, 3.1 mmol) was added slowly. The resulting mixture was stirred for 2 h and was pumped to dryness to give a brown residue which was then washed three times with 5 ml of diethyl ether each time. The solid was dissolved in 30 ml of dichloromethane; the solution was filtered and then layered with 25 ml of *n*-hexane. The resulting solution was allowed to stand at -15°C to afford brownish-green crystals (0.576 g (41.0%); m.p., 171.7 – 172.0°C). Anal. Found: C, 51.99; H, 3.71. $C_{20}H_{17}O_4ClTiCr$ Calc.: C, 52.60; H, 3.75%. IR (Nujol): $\nu(\text{CO})$ 1947 (s), 1875 (s), 1839 (s) cm^{-1} .

2.4. Synthesis of $Cp_2TiBr[(OC_6H_4CH_3)Cr(CO)_3]$ (3)

$(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.244 g, 1.0 mmol) was added slowly to a solution of $Cp_2Ti(CH_3)Br$ (0.273 g, 1.0 mmol) in 30 ml of benzene at 5°C . The resulting mixture was stirred for 2 h and was pumped to dryness to give a brown residue which was washed twice with 5 ml of diethyl ether each time. The solid was then dissolved in 30 ml dichloromethane; the solution was filtered, concentrated to 25 ml and followed by layering on 50 ml of *n*-hexane. The solution was allowed to stand at -15°C for 72 h to give brownish-green crystals (0.281 g (56.1%); m.p., 179.3 – 180.3°C). Anal. Found:

C, 47.51; H, 3.49. $C_{20}H_{17}O_4BrTiCr$ Calc.: C, 47.94; H, 3.42%. IR (Nujol): $\nu(\text{CO})$ 1949 (s), 1875 (s), 1841 (s) cm^{-1} .

2.5. Synthesis of $Cp_2Ti[(OC_6H_4CH_3)Cr(CO)_3]_2$ (4)

$(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.977 g, 4.0 mmol) was added slowly to a solution of $Cp_2Ti(CH_3)_2$ (0.416 g, 2.0 mmol) in 30 ml of dichloromethane at 5°C . The resulting mixture was allowed to warm up to room temperature and was stirred for a further 2 h. The solution was then dried in vacuo and the residue was washed twice with 15 ml of diethyl ether each time. The solid was dissolved in 40 ml of dichloromethane; the solution was filtered, concentrated to 30 ml and layered with 50 ml of *n*-hexane. The resulting solution was cooled to -15°C to afford reddish-brown crystals (0.752 g (56.6%); m.p., 180.2 – 181.6°C). Anal. Found: C, 53.82; H, 3.60. $C_{30}H_{24}O_8TiCr_2$ Calc.: C, 54.23; H, 3.64%. IR (Nujol): $\nu(\text{CO})$ 1941 (s), 1857 (s), 1849 (sh) cm^{-1} .

2.6. Synthesis of $Cp_2Zr(CH_2C_6H_5)[(OC_6H_4CH_3)Cr(CO)_3]$ (5)

To a solution of $Cp_2Zr(CH_2C_6H_5)_2$ (0.202 g, 0.5 mmol) in 30 ml of dichloromethane at -10°C , $(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.122 g, 0.5 mmol) was added slowly and the resulting mixture was stirred for 2 h. The solution was dried in vacuo to give a yellowish-brown residue which was washed with 5 ml of diethyl ether. The solid was dissolved in 15 ml of dichloromethane, followed by layering on 30 ml of *n*-hexane and cooled at -15°C to give yellow crystals (0.155 g (55.4%); m.p., 146.2 – 148.9°C). Anal. Found: C, 58.09; H, 4.27. $C_{26}H_{24}O_4ZrCr$ Calc.: C, 58.36; H, 4.35%. IR (Nujol): $\nu(\text{CO})$ 1953 (s), 1881 (s), 1845 (s) cm^{-1} .

2.7. Synthesis of $Cp_2Zr[(OC_6H_4CH_3)Cr(CO)_3]_2$ (6)

To a solution of $Cp_2Zr(CH_2C_6H_5)_2$ (0.403 g, 1.0 mmol) in 30 ml of dichloromethane at room temperature, $(\text{HO}C_6H_4CH_3)Cr(CO)_3$ (0.488 g, 2.0 mmol) was added slowly and the mixture was stirred for 1 h. The solution was dried in vacuo and the residue was washed twice with 5 ml of diethyl ether each time. The solid was dissolved in 30 ml of dichloromethane; the solution was filtered, concentrated to 20 ml and layered with 50 ml of *n*-hexane. The solution was allowed to stand at -15°C for 48 h to afford yellow crystals (0.472 g (47.2%); m.p., 205.3 – 206.7°C). Anal. Found: C, 50.71; H, 3.47. $C_{30}H_{24}O_8ZrCr_2$ Calc.: C, 50.91; H, 3.42%. IR (Nujol): $\nu(\text{CO})$ 1954 (s), 1867 (s), 1848 (sh) cm^{-1} .

2.8. Physical measurements

^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 ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal reference. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument. IR spectra were recorded on a Hitachi 270-30 spectrometer in the region of $4000\text{--}400\text{ cm}^{-1}$; the peak positions were calibrated with the 1601.4 cm^{-1} peak of polystyrene. Melting points were measured under a dry dinitrogen atmosphere using a Büchi 535 instrument and were not corrected.

2.9. Crystal structure determinations

A brownish-green crystal of **3** of size $0.40\text{ mm} \times 0.50\text{ mm} \times 0.65\text{ mm}$ and a reddish-brown crystal of **4** of size $0.40\text{ mm} \times 0.50\text{ mm} \times 0.50\text{ mm}$ were used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVax 3100-80 computer. The positions of heavy atoms for each structure were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms were considered as the riding atom on carbon atom with a C–H bond length of 0.96 \AA , and the hydrogen atom temperature factors were fixed at 0.08 . The hydrogen atoms were included for refinements in the final cycles. The crystallographic data of **3** and **4** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterizations

The bimetallic complexes $\text{Cp}_2\text{MX}[(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3]$ were synthesized by the method of dealkylation from Group 4 metallocene alkyl derivatives with $(\text{HOC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$ according to Eq. (1). The monosubstituted complexes **1**, **2**, **3** and **5** are less stable than the disubstituted complexes **4** and **6** and tends to decompose for prolonged manipulations, especially for the **1** and **5** which bear a methyl or a benzyl group on the Group 4 metal center. On the contrary, the disubstituted titanium complex **4** is stable in air for days.

The IR spectra for **1–6** in the carbonyl region reveal one high energy band around 1950 cm^{-1} and two bands or one band with a shoulder in the region between 1880 and 1840 cm^{-1} [5a,b,11]. These bands

Table 1
Crystallographic data of **3** and **4**

	3	4
Formula	$\text{C}_{20}\text{H}_{17}\text{O}_4\text{BrTiCr}$	$\text{C}_{30}\text{H}_{24}\text{O}_8\text{TiCr}_2$
Formula weight	501.1	664.4
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (\AA)	7.682(2)	7.626(3)
b (\AA)	10.262(3)	41.70(3)
c (\AA)	13.838(4)	18.287(7)
α ($^\circ$)	109.43(2)	
β ($^\circ$)	100.33(2)	92.01(3)
γ ($^\circ$)	100.10(2)	
V (\AA^3)	979.0(4)	5812(5)
z	2	8
D_{calc} (g cm^{-3})	1.700	1.519
λ (Mo $\text{K}\alpha$) (\AA)	0.71073	0.71073
Absorption coefficient (mm^{-1})	3.026	1.052
Range ($^\circ$)	3.0–50	3.0–55
Scan type	$\theta\text{--}2\theta$	$\theta\text{--}2\theta$
Number of reflections collected	3738	12163
Number of independent reflections	3455 ($R_{\text{int}} = 1.19\%$)	11000 ($R_{\text{int}} = 3.17\%$)
Number of observed reflections	2313 ($I > 3\sigma(I)$)	6207 ($I > 2\sigma(I)$)
Number of N_{params} refined parameters	244	739
R^a for significant reflections	0.072	0.050
R_w^b for significant reflections	0.090	0.062
Goodness of Fit c	1.25	1.25

$^a R = [\sum(F_o - F_c) / \sum F_o]$.

$^b R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$.

c The goodness of fit equals $[\sum w(F_o - F_c)^2 / (N_{\text{reflns}} - N_{\text{params}})]^{1/2}$.

are not very different from the $\nu(\text{CO})$ of $(\text{HOC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$ of 1948, 1882 and 1801 cm^{-1} except that the lowest energy band of **1–6** shifts to a higher energy around 1840 cm^{-1} .

The ^1H and ^{13}C NMR data are listed in Tables 2 and 3. The ^1H chemical shifts of Cp rings for **1** and **5**, which bear an alkyl group on the Group 4 metal center, appear relatively upfield compared with other complexes, and this phenomenon reflects much better donating abilities of alkyl groups towards Group 4 metals [12]. The overall order of donating abilities is $\text{X} = \text{R} \gg [(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3] > \text{Cl} > \text{Br}$ [5a,b]. The ^{13}C chemical shifts of Cp rings behave similarly. For the (arene) $\text{Cr}(\text{CO})_3$ moieties, the ^1H and ^{13}C chemical shifts of CH_3 , the ^1H chemical shifts of protons *ortho* to CH_3 , and the ^{13}C chemical shifts of carbonyls are not sensitive towards the change in X group on the Group 4 metal center. However, the ^1H chemical shifts of protons *ortho* to the oxygen donor in **1–6** shift upfield significantly from 5.11 ppm for $(\text{HOC}_6\text{H}_4\text{--}$

Table 2
 ^1H NMR data of complexes 1–6 and $(\text{HO}C_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$ in CDCl_3

Complex	M	X	δ (ppm)				
			$\eta^5\text{-C}_5\text{H}_5$	$\eta^6\text{-C}_6\text{H}_4$	CH_3	CH_2	C_6H_5
1	Ti	CH_3	6.06 (s)	4.53 (d) 5.38 (d)	2.01 (s) 0.83 (s)		
2	Ti	Cl	6.43 (s)	4.90 (d) 5.42 (d)	2.03 (s)		
3	Ti	Br	6.48 (s)	4.92 (d) 5.41 (d)	2.05 (s)		
4	Ti	$(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$	6.36 (s)	4.99 (d) 5.54 (d)	2.08 (s)		
5	Zr	$\text{CH}_2\text{C}_6\text{H}_5$	6.07 (s)	4.80 (d) 5.38 (d)	2.05 (s)	2.39 (s)	6.86 (m) 7.21 (m)
6	Zr	$(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$	6.41 (s)	4.94 (d) 5.47 (d)	2.07 (s)		
		$(\text{HO}C_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$		4.26 (s, 1H) 5.11 (d, 2H) 5.42 (d, 2H)	2.05 (s)		

$\text{CH}_3)\text{Cr}(\text{CO})_3$ to the range between 4.99 and 4.53 ppm. The most dramatic change is found for **1** ($\text{M} = \text{Ti}$; $\text{X} = \text{CH}_3$) at 4.53 ppm and less so for **5** ($\text{M} = \text{Zr}$; $\text{X} = \text{CH}_2\text{C}_6\text{H}_5$) at 4.80 ppm. Geometrically the protons *ortho* to the oxo substituent point towards the Group 4 metal and the ^1H chemical shifts of these protons might be affected by both Ti and Cr metals and also by Cp rings. However, the roles of the alkyl group in **1** and **5** in the dramatic changes in the ^1H

chemical shifts of the *ortho* protons is not clear. Yet, the changes are parallel to the also relatively upfield chemical shifts of the protons of Cp in complexes.

3.2. The molecular structures of **3** and **4**

The atomic coordinates and equivalent isotropic displacement coefficients of **3** and **4** are listed in Tables 4 and 5 and the molecular structures are shown in Figs. 1

Table 3
 ^{13}C NMR data of 1–6 in CDCl_3

Complex	M	X	δ (ppm)					
			CO	$\eta^5\text{-C}_5\text{H}_5$	$\eta^6\text{-C}_6\text{H}_4$	CH_3	CH_2	C_6H_5
1	Ti	CH_3	235.3	113.7	82.2 97.5 99.6 151.6	19.9 40.6		
2	Ti	Cl	235.0	118.5	82.4 96.9 100.5 152.0	19.9		
3	Ti	Br	235.1	118.2	82.2 96.8 100.7 152.1	19.9		
4	Ti	$(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$	235.4	117.3	84.1 97.6 100.6 151.7	19.8		
5	Zr	$\text{CH}_2\text{C}_6\text{H}_5$	235.0	112.5	83.7 96.5 101.1 145.7	19.8	52.2	121.3 126.7 128.1 151.7
6	Zr	$(\text{OC}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3$	235.1	114.3	83.8 97.0 101.2 146.9	19.9		

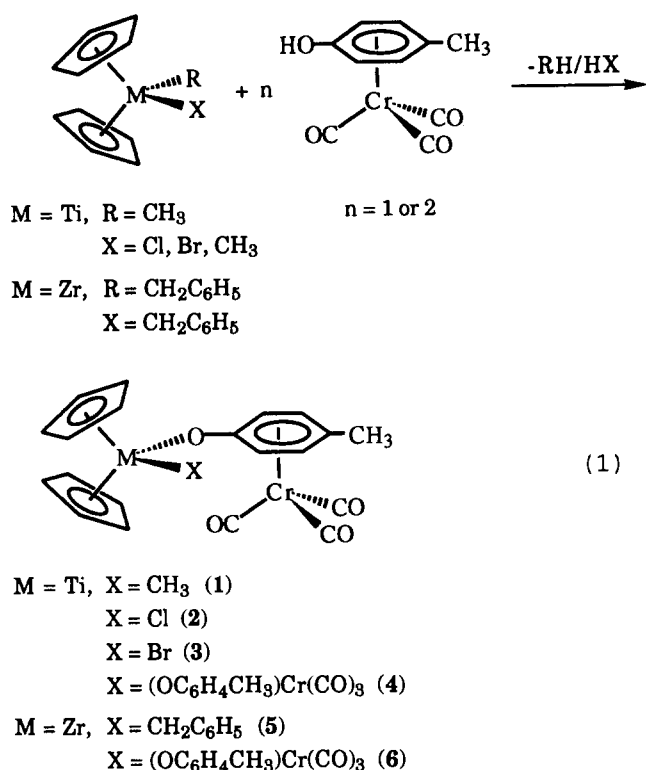


Table 4
Atomic coordinates and equivalent isotropic displacement coefficients of **3**

Atom	x	y	z	U_{eq} (\AA^2)
Ti	0.5831(2)	0.8675(1)	0.2319(1)	0.034(1)
Cr	0.1242(2)	0.4469(1)	0.2478(1)	0.034(1)
Br	0.3911(2)	1.0218(1)	0.3257(1)	0.071(1)
O	0.4328(7)	0.6936(5)	0.2234(4)	0.047(2)
O(18)	0.0390(11)	0.1644(7)	0.0723(6)	0.089(4)
O(19)	-0.2241(10)	0.3487(8)	0.2984(7)	0.086(4)
O(20)	-0.0659(14)	0.5625(8)	0.0994(6)	0.104(5)
C(1)	0.7460(14)	0.8980(13)	0.4042(7)	0.070(5)
C(2)	0.7962(14)	1.0266(12)	0.3940(8)	0.072(5)
C(3)	0.8911(13)	1.0082(10)	0.3128(8)	0.067(5)
C(4)	0.8900(13)	0.8621(11)	0.2745(9)	0.070(5)
C(5)	0.8070(13)	0.7988(11)	0.3330(8)	0.065(5)
C(6)	0.3900(23)	0.8919(28)	0.0882(11)	0.122(11)
C(7)	0.5574(30)	0.9836(15)	0.1131(9)	0.103(8)
C(8)	0.6767(17)	0.9124(19)	0.0903(10)	0.093(7)
C(9)	0.5978(30)	0.7709(17)	0.0568(9)	0.108(9)
C(10)	0.4153(28)	0.7571(21)	0.0517(10)	0.119(8)
C(11)	0.3895(10)	0.6178(7)	0.2795(6)	0.039(3)
C(12)	0.4250(10)	0.4820(7)	0.2590(6)	0.040(3)
C(13)	0.3756(9)	0.3996(8)	0.3173(6)	0.039(3)
C(14)	0.2868(11)	0.4480(8)	0.3985(6)	0.042(3)
C(15)	0.2468(11)	0.5829(7)	0.4165(6)	0.043(3)
C(16)	0.2925(10)	0.6648(8)	0.3576(6)	0.043(3)
C(17)	0.2374(12)	0.3625(9)	0.4635(7)	0.053(4)
C(18)	0.0744(12)	0.2733(9)	0.1386(7)	0.051(4)
C(19)	-0.0907(11)	0.3874(9)	0.2786(7)	0.050(4)
C(20)	0.0075(13)	0.5166(9)	0.1575(8)	0.059(4)

and **2**. The selected bond lengths and bond angles for **3** and **4** are listed in Table 6. For **3**, the Ti–Cp distances and the Cp–Ti–Cp angle are normal compared with the titanocene complexes [13]. However the Ti–O distance at 1.903 Å is long compared with the Ti–O(alkoxide) and the Ti–O(aryl) distances around 1.85 Å [14]. This distance is even comparable with or just somewhat shorter than the usual Zr–O (alkoxide) and Zr–O (aryl) distances ranged from 1.900 to 2.000 Å [15]. For the complex $\text{Cp}_2\text{TiBr}[(\text{OCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3]$ [5a] in which the phenyl ring and the oxygen donor are mediated by a CH_2 group, the Ti–Br distance at 2.558(1) Å is about the same as the value of 2.550(2) Å in **3**. However, the Ti–O distance at 1.822(3) Å in $\text{Cp}_2\text{TiBr}[(\text{OCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3]$ is substantially shorter than the Ti–O distance in **3** by 0.08 Å. The long Ti–O distance suggests a severely close contact between the titanocene and the (arene) $\text{Cr}(\text{CO})_3$ moieties. For **4**, two independent molecules are found in a unit cell and labeled as structures **4** and **4'**. In **4** and **4'**, the average Ti–Cp distance at 2.082 Å is somewhat longer than the value of 2.053 Å in **3** and the O(1)–Ti–O(2) angles at 98.4(2) and 96.6(2)° are larger than the Br–Ti–O angle in **3** at 94.1(2)°. The Cp–Ti–Cp angles at 131.6 and 131.0° are somewhat smaller than 131.7° in **3**, but the differences are not significant. The two Ti–O distances in **4** or **4'** are inequivalent with an average of 1.927 Å, which is even longer than the distance in **3** by 0.024 Å. Much more severely steric crowdedness is suggested for **4**.

For (arene) $\text{Cr}(\text{CO})_3$ moieties, several important features are observed. The two phenyl rings in **4** and **4'** are tilted in opposite directions from the O(1)–Ti–O(2) plane with angles of 39.5 and 37.5° for **4** and angles of 37.9 and 43.1° for **4'**. The angle between two phenyl rings is 75.0° for **4** and 75.3° for **4'**. The Cr-carbonyl tripods are on the opposite side from the tilting direction of the phenyl rings and therefore two Cr-carbonyl tripods located in opposite directions. However, in the similar complex $\text{Cp}_2\text{Zr}[(\text{OC}_6\text{H}_5)\text{Cr}(\text{CO})_3]_2$ [5a], in which there is a larger Zr core and less steric crowdedness among the zirconocene and (arene) $\text{Cr}(\text{CO})_3$ moieties, the phenyl rings are tilting in the same direction with both Cr-carbonyl tripods located on the same side. The reason that the two phenyl rings bend away in **4** and **4'** is just to avoid the close contact between two inner *ortho* hydrogen atoms in the (arene) $\text{Cr}(\text{CO})_3$ moieties. The distances between two inner hydrogen atoms at 2.540 Å (H(12A)–H(26A) in **4**) and 2.203 Å (H(12B)–H(22B) in **4'**) are about similar to or somewhat shorter than the van der Waals distance of 2.40 Å of two hydrogen atoms [16]. In **3**, the phenyl ring also bends away from the O(1)–Ti–Br plane by 34.1°. In comparison with the O–C(aryl) distances at 1.37 ± 0.01 Å in the Ti–OAr complexes [14b,f], the slightly short O–C(aryl) distance at 1.312(11) Å for **3** and at 1.336 Å

Table 5
Atomic coordinates and equivalent isotropic displacement coefficients of **4**

Atom	x	y	z	U_{eq} (\AA^2)
Ti	0.7548(1)	0.6561(1)	0.8872(2)	0.042(1)
Cr(1)	0.5620(1)	0.5640(1)	1.0506(1)	0.045(1)
Cr(2)	0.6637(1)	0.6992(1)	1.1480(1)	0.046(1)
O(1)	0.6685(5)	0.6151(1)	0.9208(2)	0.067(2)
O(2)	0.7454(5)	0.6792(2)	0.9773(2)	0.068(2)
O(18)	0.2300(7)	0.5586(2)	0.9588(3)	0.119(4)
O(19)	0.3623(10)	0.6113(2)	1.1375(4)	0.135(3)
O(20)	0.4362(8)	0.5121(2)	1.1475(3)	0.095(3)
O(28)	0.9870(7)	0.6595(2)	1.1477(4)	0.114(3)
O(29)	0.8595(7)	0.7450(2)	1.2467(3)	0.084(2)
O(30)	0.5466(10)	0.6607(2)	1.2748(3)	0.126(3)
C(1)	0.4849(9)	0.6841(3)	0.8650(4)	0.074(3)
C(2)	0.4573(8)	0.6532(2)	0.8415(4)	0.071(3)
C(3)	0.5628(9)	0.6470(3)	0.7840(4)	0.077(4)
C(4)	0.6519(10)	0.6741(3)	0.7697(4)	0.084(4)
C(5)	0.6087(11)	0.6971(3)	0.8206(6)	0.093(4)
C(6)	1.0466(8)	0.6421(2)	0.9329(4)	0.064(3)
C(7)	1.0125(8)	0.6235(2)	0.8733(5)	0.077(3)
C(8)	0.9936(8)	0.6432(2)	0.8131(4)	0.071(3)
C(9)	1.0163(8)	0.6749(2)	0.8355(4)	0.075(3)
C(10)	1.0512(8)	0.6735(2)	0.9117(5)	0.071(3)
C(11)	0.7231(7)	0.5930(2)	0.9687(3)	0.050(2)
C(12)	0.7787(8)	0.6006(2)	1.0403(3)	0.058(2)
C(13)	0.8359(8)	0.5756(2)	1.0892(3)	0.061(3)
C(14)	0.8364(8)	0.5436(2)	1.0695(3)	0.057(2)
C(15)	0.7730(7)	0.5365(2)	0.9970(3)	0.054(2)
C(16)	0.7147(8)	0.5601(2)	0.9496(3)	0.056(2)
C(17)	0.8993(10)	0.5178(2)	1.1200(4)	0.081(3)
C(18)	0.3620(10)	0.5601(2)	0.9940(4)	0.070(3)
C(19)	0.4437(11)	0.5919(2)	1.1055(4)	0.077(3)
C(20)	0.4835(9)	0.5316(2)	1.1091(4)	0.063(3)
C(21)	0.6390(7)	0.6944(2)	1.0220(3)	0.047(2)
C(22)	0.6738(8)	0.7262(2)	1.0425(3)	0.057(2)
C(23)	0.5639(10)	0.7426(2)	1.0905(3)	0.064(3)
C(24)	0.4242(10)	0.7279(3)	1.1208(4)	0.078(4)
C(25)	0.3928(8)	0.6956(2)	1.1024(3)	0.069(3)
C(26)	0.4993(7)	0.6782(2)	1.0535(3)	0.053(2)
C(27)	0.2943(12)	0.7438(3)	1.1690(5)	0.129(6)
C(28)	0.8623(10)	0.6747(2)	1.1465(4)	0.068(3)
C(29)	0.7835(9)	0.7269(2)	1.2093(3)	0.054(2)
C(30)	0.5907(11)	0.6763(2)	1.2259(4)	0.076(3)
Ti'	0.2383(1)	0.5757(1)	0.3808(1)	0.031(1)
Cr(1')	0.0206(1)	0.5613(1)	0.6397(1)	0.038(1)
Cr(2')	0.0545(1)	0.6851(1)	0.4858(1)	0.041(1)
O(1')	0.1479(5)	0.5568(1)	0.4690(2)	0.049(1)
O(2')	0.2106(5)	0.6194(1)	0.4093(2)	0.046(1)
O(18')	-0.2185(8)	0.6181(2)	0.6332(3)	0.098(3)
O(19')	-0.2798(7)	0.5269(2)	0.5687(3)	0.095(3)
O(20')	-0.1311(7)	0.5448(2)	0.7824(3)	0.100(3)
O(28')	0.4004(7)	0.6662(2)	0.5556(3)	0.104(3)
O(29')	0.1792(10)	0.7528(2)	0.4776(4)	0.126(3)
O(30')	-0.0722(9)	0.6977(2)	0.6351(3)	0.116(3)
C(1')	-0.0347(9)	0.5868(2)	0.3137(4)	0.070(3)
C(2')	0.0948(10)	0.5863(3)	0.2650(3)	0.074(3)
C(3')	0.1579(13)	0.5563(3)	0.2624(4)	0.080(4)
C(4')	0.0689(13)	0.5382(2)	0.3143(5)	0.090(4)
C(5')	-0.0519(8)	0.5581(2)	0.3438(3)	0.064(3)
C(6')	0.5235(7)	0.5795(2)	0.4431(3)	0.055(3)
C(7')	0.4962(8)	0.5476(2)	0.4249(4)	0.063(3)
C(8')	0.4876(8)	0.5463(2)	0.3479(4)	0.073(3)

Table 5 (continued)

Atom	x	y	z	U_{eq} (\AA^2)
C(9')	0.5074(8)	0.5770(2)	0.3205(3)	0.066(3)
C(10')	0.5289(7)	0.5973(2)	0.3792(4)	0.057(2)
C(11')	0.1965(7)	0.5580(2)	0.5399(3)	0.044(2)
C(12')	0.2259(8)	0.5873(2)	0.5771(3)	0.050(2)
C(13')	0.2756(7)	0.5878(2)	0.6526(3)	0.051(2)
C(14')	0.2930(8)	0.5593(2)	0.6920(3)	0.053(2)
C(15')	0.2561(7)	0.5301(2)	0.6565(3)	0.046(2)
C(16')	0.2057(7)	0.5297(2)	0.5811(3)	0.047(2)
C(17')	0.3526(10)	0.5592(2)	0.7723(3)	0.076(3)
C(18')	-0.1233(10)	0.5964(2)	0.6362(3)	0.061(2)
C(19')	-0.1628(9)	0.5399(2)	0.5957(3)	0.053(2)
C(20')	-0.0723(9)	0.5510(2)	0.7278(3)	0.059(2)
C(21')	0.0809(7)	0.6412(2)	0.4115(3)	0.041(2)
C(22')	-0.0587(7)	0.6367(2)	0.4594(3)	0.046(2)
C(23')	-0.1937(8)	0.6602(2)	0.4598(3)	0.054(2)
C(24')	-0.1942(9)	0.6874(2)	0.4157(3)	0.064(3)
C(25')	-0.0492(10)	0.6915(2)	0.3717(3)	0.062(2)
C(26')	0.0890(8)	0.6694(2)	0.3701(3)	0.052(2)
C(27')	-0.3426(9)	0.7106(2)	0.4135(4)	0.078(3)
C(28')	0.2698(9)	0.6739(2)	0.5287(4)	0.062(3)
C(29')	0.1271(10)	0.7268(2)	0.4818(4)	0.065(3)
C(30')	-0.0236(9)	0.6926(2)	0.5781(4)	0.067(3)

(average distance) for **4** suggests some π bonding character developed between O and C(aryl) atoms.

The molecular orbital calculation has shown a low rotational barrier between eclipsed conformation **I** and staggered conformation **II** with the staggered form favored by 0.3 kcal mol⁻¹. For monosubstituted (arene)Cr(CO)₃ complexes, the conformation would be *syn*-eclipsed conformation **III**, *anti*-eclipsed conformation **IV** or staggered conformation **V**.

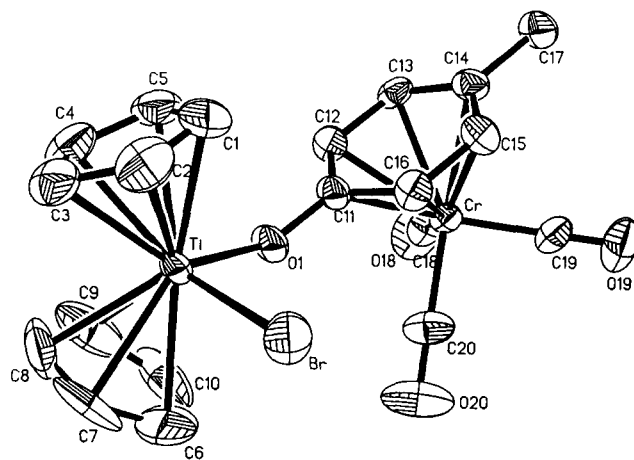


Fig. 1. The molecular structure of **3**. Hydrogen atoms are omitted for clarity.

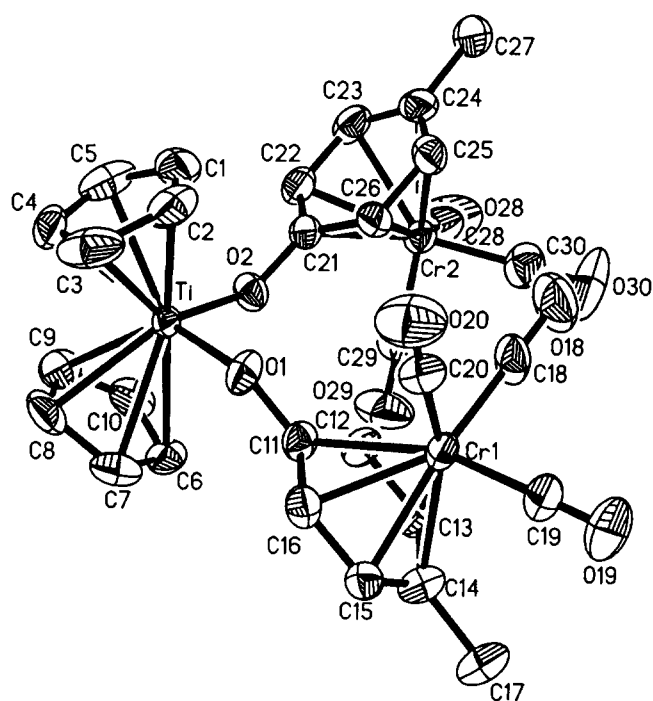


Fig. 2. The molecular structure of **4** (only structure **4** is shown). Hydrogen atoms are omitted for clarity.

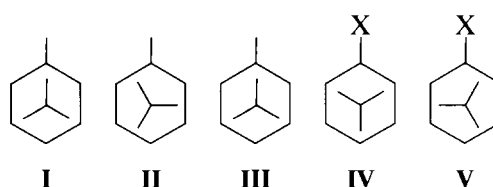
Table 6
Selected bond lengths (Å) and bond angles (°) for **3** and **4**

	3		4	
			4	4'
Bond lengths				
Ti–Br	2.550(2)	Ti–O(1)	1.941(6)	1.944(4)
Ti–O(1)	1.903(6)	Ti–O(2)	1.912(5)	1.910(5)
Ti–Cp(1)	2.056	Ti–Cp(1)	2.074	2.089
Ti–Cp(2)	2.049	Ti–Cp(2)	2.087	2.078
O–C(11)	1.312(11)	O(1)–C(11)	1.329(8)	1.336(6)
Cr–Ph	1.740	O(2)–C(21)	1.334(7)	1.343(7)
(Cr–CO) _{av}	1.827	Cr(1)–Ph(1)	1.765	1.759
(C–O) _{av}	1.150	Cr(2)–Ph(2)	1.755	1.745
		(Cr(1)–CO) _{av}	1.819	1.828
		(Cr(2)–CO) _{av}	1.825	1.840
		(Cr(1)C–O) _{av}	1.168	1.147
		(Cr(2)C–O) _{av}	1.157	1.146
Bond angles				
Br–Ti–C(1)	94.1(2)	O(1)–Ti–O(2)	98.4(2)	96.6(2)
Cp(1)–Ti–Cp(2)	131.7	Cp(1)–Ti–Cp(2)	131.6	131.0
Ti–O(1)–C(11)	143.4(4)	Ti–O(1)–C(11)	136.0(4)	134.1(4)
		Ti–O(2)–C(21)	144.2(4)	137.8(4)

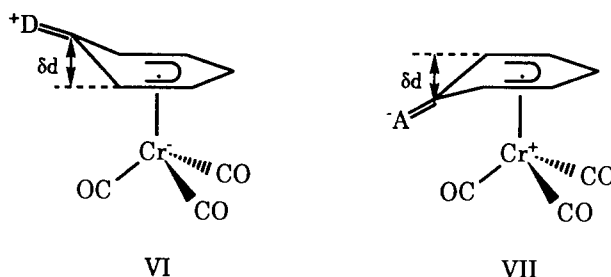
Table 7
 δd values and dihedral angles for **3** and **4**^a

	3	4		4'		Cp ₂ Zr[(OC ₆ H ₅)Cr(CO) ₃] ₂
		Ph(1)	Ph(2)	Ph(1')	Ph(2')	
$\delta d_{\text{C(OML}_n)}$ (Å)	0.087	0.075	0.076	0.075	0.067	0.096
$\delta d_{\text{C(CH}_3)}$ (Å)	0.004	0.016	0.043	–0.013	0.029	–
Dihedral angle (°)	24.4	48.3	1.2	40.5	0.4	9.4
Conformation	Staggered	<i>anti</i> -eclipsed	<i>syn</i> -eclipsed	Staggered	<i>syn</i> -eclipsed	<i>syn</i> -eclipsed

^a $\delta d = d_{\text{Cr–C}_{\text{ipso}}} - d_{\text{Cr–C(H)}_{\text{av}}}$



The *syn*-eclipsed form **III** is favored by the electron-donating substituent and the *anti*-eclipsed conformation **IV** is favored by the electron-withdrawing substituent. Furthermore the structural non-planarity of the phenyl ring in the (arene)Cr(CO)₃ complexes can be correlated to the donor–acceptor abilities of the ring substituent [4a]. With an electron-donating substituent, the *ipso* carbon is puckered away from the Cr metal center with the δd value positive (**VI**) and, with an electron-withdrawing substituent, the *ipso* carbon is puckered towards the Cr center with the δd value negative (**VII**).



In **3** and **4**, the oxo substituent is *para* to the methyl group and coordinates to the titanium metal. The δd values for *ipso* carbon atoms bonded to the two substituents and dihedral angles of the Cr–carbonyl tripods for **3** and **4** are listed in Table 7. Both oxo and CH₃ substituents are electron donating with $\delta d_{\text{C(OTiL}_n)}$ ranging from 0.067 to 0.087 Å and $\delta d_{\text{C(CH}_3)}$ ranging from –0.013 to 0.043 Å. The oxo substituent is still more electron donating than the *para* CH₃ substituent even with the oxo group bonded further to the electropositive titanium metal center. Therefore the Cr–carbonyl tripods are expected to have the *syn*-eclipsed conformation relative to the oxo substituent. Indeed, for the larger zirconium complex of Cp₂Zr[(OC₆H₅)Cr(CO)₃]₂, the *syn*-eclipsed conformation with dihedral angle skewed at 9.4° is observed. However, for **3**, the Cr–carbonyl tripod is in staggered form with the

dihedral angle of 24.4°. For **4**, one of the Cr-carbonyl tripods adopts nearly the *syn*-eclipsed conformation with a dihedral angle of 1.2° (structure **4**) and 0.4° (structure **4'**). However, another Cr-carbonyl tripod is skewed away from the oxo donor with a dihedral angle of 48.3° close to the *anti*-eclipsed form in **4** and a dihedral angle of 40.5° close to the staggered form in **4'**. The skewing away of one Cr-carbonyl tripod from the preferred *syn*-eclipsed conformation probably arises in order to avoid close contact of two inner carbonyls. The closest distances of the two oxygen atoms of the inner carbonyls are 3.504 Å (O19–O30' in **4**) and 3.502 Å (O18–O30' in **4'**) which are longer than the van der Waals distance of 2.80 Å of two oxygen atoms by only 0.7 Å. This study has revealed that the steric effect can become an important factor for the adoption of the conformation of Cr-carbonyl tripods.

Other structural features for (arene)Cr(CO)₃ moieties for **3** and **4**, such as the Cr–Ph distances, the Cr–CO distances and the Cr–O distances are rather similar for both complexes and are normal compared with other (arene)Cr(CO)₃ complexes.

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