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# Group IV metal–chromium complexes bridged by a benzoate group

Han-Mou Gau, Chi-Tain Chen, Ting-Ting Jong and Mei-Yueh Chien

Department of Chemistry, National Chung-Hsing University, Taichung 40227 (Taiwan, ROC)

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## Abstract

The complexes,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}[(\mu\text{-O}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3]$  ( $\text{X} = \text{Cl}$  (1), Br (2), or  $\text{CH}_3$  (3)), were prepared by reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}(\text{CH}_3)$  with 1 molar equivalent of  $(\text{HO}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$ . The complexes,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}[(\mu\text{-O}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3]_2$  ( $\text{M} = \text{Ti}$  (4) or  $\text{Zr}$  (5)), were obtained by reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$  with 2 molar equivalents of  $(\text{HO}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$ . IR spectra of complexes 1–4 show that the carboxylate groups coordinate to the Ti metal in monodentate mode. However, the IR spectrum of complex 5 indicates that two carboxylate groups adopt one monodentate and one bidentate attachment to Zr metal. Complex 3 crystallizes in the triclinic  $P\bar{1}$  space group with cell parameters  $a = 8.132(2)$  Å,  $b = 11.536(4)$  Å,  $c = 12.464(4)$  Å,  $\alpha = 62.37(1)^\circ$ ,  $\beta = 70.93(1)^\circ$ ,  $\gamma = 75.56(1)^\circ$ ,  $R = 0.047$  and  $R_w = 0.050$ . Complex 5 also crystallizes in the triclinic  $P\bar{1}$  space group with cell parameters  $a = 7.761(2)$  Å,  $b = 12.012(4)$  Å,  $c = 16.255(4)$  Å,  $\alpha = 103.85(1)^\circ$ ,  $\beta = 96.53(1)^\circ$ ,  $\gamma = 103.35(1)^\circ$ ,  $R = 0.039$  and  $R_w = 0.053$ . The X-ray structures of complexes 3 and 5 confirm the coordination mode of the carboxylate groups.

## 1. Introduction

The early–late heterobimetallic complexes have attracted considerable attention recently owing to the potential ability of the early transition metal to activate a small molecule such as CO on the late transition metal centers [1]. One way to prepare these heterobimetallic complexes is using difunctional ligands to bridge the two metal fragments [2]. Numerous difunctional ligands have been used for this purpose [3–10], yet the arene system  $\text{C}_6\text{H}_5\text{X}$  with  $\text{X} = \text{CH}_2\text{OH}$ ,  $\text{COOH}$ , or  $\text{OH}$  as the difunctional ligands has attracted little attention. These arene systems are suitable ligands for bridging Group VI transition metals through  $\pi$ -complexation by the phenyl ring and Group IV metals through the oxygen donors of the X substituents. One advantage of this type of ligand is the availability of the  $(\text{arene})\text{Cr}(\text{CO})_3$  complexes [11] which have been known for more than two decades. Another advantage is the ability of these  $(\text{arene})\text{Cr}(\text{CO})_3$  complexes to react with many early transition metal complexes such as metallocene complexes, mono-cyclo-

pentadienyl complexes, and transition metal complexes without cyclopentadienyl ligands.

We have already successfully demonstrated the reaction between  $(\text{HOCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3$  and Group IV metallocenes [12]. Here we report the synthesis, characterization and structure of the complexes,  $\text{Cp}_2\text{MX}[(\mu\text{-O}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{M} = \text{Ti}$ ,  $\text{X} = \text{Cl}$  (1), Br (2),  $\text{CH}_3$  (3),  $(\text{O}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$  (4);  $\text{M} = \text{Zr}$ ,  $\text{X} = (\text{O}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$  (5)), which are prepared by reaction of  $(\text{HO}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$  with group IV metallocenes. The IR spectra and X-ray structure show the carboxylate groups bonded to the titanium metal in monodentate mode and to the zirconium metal in mono- and bidentate modes.

## 2. Experimental section

### 2.1. Reagents and general techniques

The compounds  $(\text{HO}_2\text{CC}_6\text{H}_5)\text{Cr}(\text{CO})_3$  [11],  $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{Cl}$  [13],  $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{Br}$  [13],  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$  [14], and  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  [15] were prepared according to literature procedures. Solvents were dried by refluxing for at least 24 h over  $\text{P}_2\text{O}_5$  (dichloromethane) or sodium/benzophenone (toluene, diethyl ether, hexane); all solvents were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecu-

Correspondence to: Dr. H.-M. Gau.

lar sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

### 2.2. Synthesis of $Cp_2TiCl[(\mu-O_2CC_6H_5)Cr(CO)_3]$ (1)

A mixture of  $Cp_2Ti(CH_3)Cl$  (0.690 g, 3.02 mmol) and  $(HO_2CC_6H_5)Cr(CO)_3$  (0.779 g, 3.02 mmol) in 60 ml of diethyl ether was stirred at room temperature under a dry dinitrogen atmosphere for 72 h. The resulting cloudy solution was filtered and the precipitate was dissolved in 40 ml of dichloromethane to give a red solution. Hexane (40 ml) was layered on this solution to afford an impure red crystalline material (0.40 g, 28.2%). IR (Nujol mull): 1971s, 1875s, 1641s, 1518w, 1503w, 1413w, 1314s, 1280sh, 1143m, 1136sh, 1068w, 1044w, 1011m, 855m, 822s, 771m, 732w, 660s, 627s, 620sh, 573m, 528m, 474w, 408m  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.61 (s, 10H); 6.02 (m, 2H); 5.52 (m, 1H); 5.27 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  232.4 (CO); 119.7 (Cp); 96.1, 95.6, 95.1, 90.3 ppm.

### 2.3. Synthesis of $Cp_2TiBr[(\mu-O_2CC_6H_5)Cr(CO)_3]$ (2)

A mixture of  $Cp_2Ti(CH_3)Br$  (0.730 g, 2.67 mmol) and  $(HO_2CC_6H_5)Cr(CO)_3$  (0.690 g, 2.67 mmol) in 80 ml of diethyl ether was stirred at room temperature under a dry dinitrogen atmosphere for 48 h. The red precipitate was filtered off and was crystallized in dichloromethane/hexane (40 ml/50 ml) to afford a red crystalline material (0.78 g, 50.8%). Anal. Found: C, 45.63; H, 2.93.  $C_{20}H_{15}O_5BrTiCr$  calc.: C, 46.63; H, 2.93%. IR (Nujol mull): 1971s, 1875s, 1641s, 1518w, 1503w, 1413w, 1314s, 1277sh, 1140m, 1123sh, 1065vw, 1044vw, 1008w, 855vw, 825s, 771w, 717w, 660m, 627s, 618sh, 573m, 528m, 471w  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.66 (s, 10H); 6.00 (m, 2H); 5.52 (m, 1H); 5.27 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  231.7 (CO); 169.8 ( $CO_2$ ); 119.3 (Cp); 96.2, 95.5, 95.0, 90.2 ppm.

### 2.4. Synthesis of $Cp_2Ti(CH_3)[(\mu-O_2CC_6H_5)Cr(CO)_3]$ (3)

$Cp_2Ti(CH_3)_2$  (0.416 g, 2.0 mmol) and  $(HO_2CC_6H_5)Cr(CO)_3$  (0.516 g, 2.0 mmol) were placed in a reaction vessel which was shielded from light and 80 ml of toluene at 0°C was transferred via a cannula. The resulting solution was stirred at 0°C for 1 h and then warmed slowly to room temperature. The reaction solution was concentrated to 40 ml and cooled to -15°C to afford orange-red crystals (0.49 g, 54.4%), m.p. 143.6–148.0°C dec. Anal. Found: C, 56.01; H, 4.05.  $C_{21}H_{18}O_5TiCr$  calc.: C, 56.02; H, 4.03%. IR (Nujol mull): 1934w, 1975sh, 1644s, 1521w, 1503w, 1410w, 1326s, 1278m, 1143m, 1068w, 1044m, 1017sh, 921w, 888w, 816s, 774m, 660s, 627sh, 600m, 570m, 528m, 480m, 408m  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.26 (s, 10H); 5.80 (m, 2H); 5.47 (m, 1H); 5.22 (m, 2H); 1.04 (s, 3H)

ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  232.5 (CO); 168.8 ( $CO_2$ ); 115.1 (Cp); 95.7, 94.9, 90.1, 46.5 ( $CH_3$ ) ppm.

### 2.5. Synthesis of $Cp_2Ti[(\mu-O_2CC_6H_5)Cr(CO)_3]_2$ (4)

$Cp_2Ti(CH_3)_2$  (0.208 g, 1.0 mmol) and  $(HO_2CC_6H_5)Cr(CO)_3$  (0.516 g, 2.0 mmol) were placed in a reaction vessel which was shielded from light and 40 ml of dichloromethane were added. The reaction mixture was stirred at room temperature under a dry dinitrogen atmosphere for 4 h. The resulting solution was concentrated to 30 ml and then layered with 30 ml of hexane giving golden-yellow crystals (0.27 g, 39.0%), m.p. 183.5–188.3°C dec. Anal. Found: C, 51.52; H, 2.99.  $C_{30}H_{20}O_{10}TiCr_2$  calc.: C, 52.04; H, 2.91%. IR (Nujol mull): 1969s, 1878sh, 1641s, 1524w, 1503w, 1413m, 1341s, 1308sh, 1143s, 1044m, 1038m, 891w, 867w, 822s, 771m, 657s, 627sh, 567s, 528m, 477m, 426m  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.66 (s, 10H); 6.13 (m, 4H); 5.56 (m, 2H); 5.38 (m, 4H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  232.6 (CO); 169.8 ( $CO_2$ ); 119.5 (Cp); 95.5, 95.0, 94.8, 90.9 ppm.

### 2.6. Synthesis of $Cp_2Zr[(\mu-O_2CC_6H_5)Cr(CO)_3]_2$ (5)

A mixture of  $Cp_2Zr(CH_3)_2$  (0.251 g, 1.0 mmol) and  $(HO_2CC_6H_5)Cr(CO)_3$  (0.516 g, 2.0 mmol) in 40 ml of dichloromethane was stirred at room temperature under a dry dinitrogen atmosphere for 4 h. The resulting solution was concentrated to 30 ml and then 30 ml of hexane was slowly layered on to give red crystals (0.375 g, 51.0%), m.p. 180.5–190.8°C dec. Anal. Found: C, 48.97; H, 2.84.  $C_{30}H_{20}O_{10}ZrCr_2$  calc.: C, 48.98; H, 2.74%. IR (Nujol mull): 1983sh, 1896br, 1641s, 1542m, 1524m, 1494w, 1425m, 1377m, 1329s, 1146sh, 1047w, 1011s, 990w, 891w, 864m, 774m, 735w, 720w, 690s, 660s, 651s, 555s, 525s, 477m  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.39 (s, 10H); 6.22 (m, 4H); 5.62 (m, 2H); 5.32 (m, 4H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  232.0 (CO); 173.4 ( $CO_2$ ); 95.8, 95.4, 91.7, 89.6 ppm.

### 2.7. 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  $^1H$  and  $^{13}C$  chemical shifts were measured relative to TMS as the internal reference. Melting points were measured under a dry dinitrogen atmosphere using a Büchi 535 instrument and were not corrected. Elemental analyses of the complexes were performed using a Heraeus CHN-O-RAPID instrument.

TABLE 1. Crystallographic data of complexes **3** and **5**

Complex	<b>3</b>	<b>5</b>
Formula	C <sub>21</sub> H <sub>18</sub> O <sub>5</sub> TiCr	C <sub>30</sub> H <sub>20</sub> O <sub>10</sub> Cr <sub>2</sub> Zr
FW	450.3	735.7
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.113(2)	7.761(3)
<i>b</i> (Å)	11.536(4)	12.012(4)
<i>c</i> (Å)	12.465(4)	16.255(5)
$\alpha$ (°)	62.37(1)	103.85(1)
$\beta$ (°)	70.93(1)	96.53(1)
$\gamma$ (°)	75.56(1)	103.35(1)
<i>V</i> (Å <sup>3</sup> )	970.3(5)	1408.4(8)
<i>z</i>	2	2
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.541	1.735
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71069	0.71069
Absorption coefficient (mm <sup>-1</sup> )	0.982	1.154
Range (°)	3.5–60.0	3.5–60.0
Scan type	$\theta$ – $2\theta$	$\theta$ – $2\theta$
Reflection collected	3709	6998
Independent reflection	3441 ( <i>R</i> <sub>int</sub> = 2.93%)	6517 ( <i>R</i> <sub>int</sub> = 1.92%)
Observed reflection	2513 ( <i>I</i> > 2 $\sigma$ <i>I</i> )	5712 ( <i>I</i> > 3 $\sigma$ <i>I</i> )
No. of refined parameters	321	463
<i>R</i> <sup>a</sup> for significant reflections	0.047	0.039
<i>R</i> <sub>w</sub> <sup>b</sup> for significant reflections	0.050	0.053
GoF <sup>c</sup>	1.15	1.49

<sup>a</sup>  $R = [\sum(F_o - F_c)/\sum F_o]$ . <sup>b</sup>  $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ . <sup>c</sup> GoF =  $[\sum w(F_o - F_c)^2 / (N_{\text{refl}} - N_{\text{params}})]^{1/2}$ .

### 2.8. Crystal structure determination

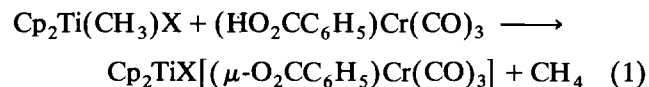
An orange crystal of **3** (0.30 × 0.20 × 0.10 mm) and a red crystal of **5** (0.80 × 0.60 × 0.40 mm) were used for the X-ray structural analyses. The diffraction intensi-

ties were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å. All calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVax 3100 computer. The structures were solved by the direct method and refined by the full-matrix least-squares method. The crystallographic data of complexes **3** and **5** are summarized in Table 1.

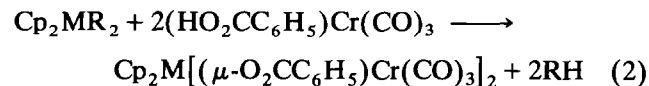
## 3. Results and discussion

### 3.1. Synthesis and characterization

The complexes, Cp<sub>2</sub>TiX[( $\mu$ -O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>] (X = Cl (**1**), Br (**2**), or CH<sub>3</sub> (**3**)), were prepared by demethylation of Cp<sub>2</sub>Ti(CH<sub>3</sub>)X with 1 molar equivalent of (HO<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub> in diethyl ether or toluene (eqn. (1)).



Complexes **1** and **2** contain a trace of impurities and we were unable to isolate them in pure form. The elemental analysis of complex **1** was not satisfactory and is not reported. The complexes, Cp<sub>2</sub>M[( $\mu$ -O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>]<sub>2</sub> (M = Ti (**4**) or Zr (**5**)), were prepared by de-alkylation of group IV metallocene dibenzyl or dimethyl with 2 molar equivalents of (HO<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub> in dichloromethane (eqn. (2)).



Complexes **1** and **2** are less soluble in benzene or dichloromethane than complexes **3**–**5**. These complexes in the solid state are stable in air for days.

TABLE 2. CO and CO<sub>2</sub> IR stretching bands of complexes **1**–**5**<sup>a</sup>

Vibration mode	Complex				
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
$\nu(\text{CO})$	1971	1971	1974	1972	1983
	1875	1875	1895	1901	1963
			1875	1881	1922
					1914
					1896
Monodentate CO <sub>2</sub>					1876
$\nu(\text{CO}_2)$ (asym)	1641	1641	1644	1641	1641
$\nu(\text{CO}_2)$ (sym)	1314	1314	1326	1341	1329
Bidentate CO <sub>2</sub>					
$\nu(\text{CO}_2)$ (asym)					1542
$\nu(\text{CO}_2)$ (sym)					1377

<sup>a</sup> Nujol mulls between KBr plates. Additional frequencies are listed in the Experimental section.

IR stretching bands of carbonyl and carboxylate groups of the complexes are listed in Table 2. The mono-substituted arene chromium complexes,  $(C_6H_5X)Cr(CO)_3$ , have been studied extensively by IR spectroscopy [16] and these complexes exhibit a high energy  $\nu(CO)$  band around  $1950\text{ cm}^{-1}$  both in solid state and in solution, but one  $\nu(CO)$  band in solution and usually two  $\nu(CO)$  bands in the solid state in the region between  $1900$  and  $1850\text{ cm}^{-1}$ . In our study of the benzoate group bridged bimetallic complexes in the solid state, two  $\nu(CO)$  bands are observed for complexes **1** and **2**. However, the low energy  $\nu(CO)$  band near  $1875\text{ cm}^{-1}$  is somewhat broad and likely arises from two overlapping absorptions of similar energy. For complex **3**, three  $\nu(CO)$  bands are observed with two bands in the low energy region. For the di-substituted Ti-Cr<sub>2</sub> complex **4**, two sets of broad  $\nu(CO)$  bands are observed with a shoulder in the low energy band. For complex **5**, the IR spectrum shows two well resolved peaks in the high energy region above  $1960\text{ cm}^{-1}$  and very broad  $\nu(CO)$  bands with shoulders in the range of  $1930$ – $1850\text{ cm}^{-1}$ . This result may indicate that two  $(O_2CC_6H_5)Cr(CO)_3$  moieties in complex **5** are environmentally different in the solid state. Two sets of  $\nu(CO_2)(\text{asym})$  and  $\nu(CO_2)(\text{sym})$  for complex **5** suggests both mono- and bidentate coordination of the two carboxylate groups to achieve 18 electrons on the larger zirconium metal center [17]. For complexes **1**–**4**, the carboxylate groups are all monodentate with  $\nu(CO_2)(\text{asym})$  near  $1640\text{ cm}^{-1}$  and  $\nu(CO_2)(\text{sym})$  in the range of  $1310$ – $1340\text{ cm}^{-1}$  [18].

Although the carboxylate complexes of Group IV metallocenes have been established since the 1960s, the introduction of a second metal in the carboxylate ligand has not been reported except for the Group IV metal-iron complexes we reported earlier [19]. In order to understand the effect of the second metal on the coordination of carboxylate groups to Group IV metallocenes, the  $^1H$  and  $^{13}C$  NMR of complexes **1**–**5** and other carboxylate complexes [19–24] are listed in Table 3 for the purpose of comparison. The  $^1H$  and  $^{13}C$  chemical shifts of the Cp rings for complexes **1** and **2** appear further downfield relative to the chemical shifts for complex **3**,  $Cp_2Ti(CH_3)(OC(O)C_6H_5)Cr(CO)_3$ . For the bis(carboxylato) complexes **4**,  $[Cp_2TiOC(O)C_6H_4C(O)O]_4$  [20],  $[Cp_2TiOC(O)CH=CHC(O)O]_2$  [21], and  $Cp_2Ti[(OC(O)C_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$  [19], the  $^1H$  chemical shifts of Cp rings are similar to those of complexes **1** and **2** at  $\delta$  6.60–6.70 ppm and the  $^{13}C$  chemical shifts are at  $\sim \delta$  119.0 ppm. For the bis(carboxylato) zirconocene complexes **5** and  $Cp_2Zr[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$  [19] and the mono(carboxylato) complexes  $Cp_2ZrCl(O_2CR)$  ( $R = C_6H_5, CH_3, C(CH_3)_3$  or  $Ru(CO)_2Cp$ ) [22,23], the  $^1H$

TABLE 3. The selected  $^1H$  and  $^{13}C$  NMR data of complexes **1**–**5** and related complexes <sup>a</sup>

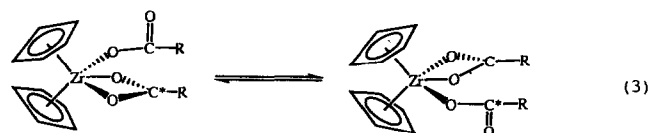
Complex	$^1H$	$^{13}C$	
	$C_5H_5$ <sup>b</sup>	$C_5H_5$ <sup>b</sup>	$CO_2$
<b>1</b>	6.61	119.7	–
<b>2</b>	6.66	119.3	169.8
<b>3</b>	6.26	115.1	168.8
<b>4</b>	6.66	119.5	169.8
<b>5</b>	6.39	114.8	173.4
$[Cp_2TiOC(O)C_6H_4C(O)O]_4$	6.72	118.8	171.7
$[Cp_2TiOC(O)CH=CHC(O)O]_2$	6.56	118.45	172.17
$Cp_2Ti[(OC(O)C_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$	6.62	118.9	169.5
$Cp_2Zr[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$	6.38	114.4	173.6
$Cp_2ZrCl[(O_2CC_6H_5)]$	6.32	114.7	171.9
$Cp_2ZrCl[(O_2CCH_3)]$	6.29	114.7	187.1
$Cp_2ZrCl[(O_2CC(CH_3)_3)]$	6.21	114.5	193.8
$Cp_2ZrCl[(O_2CRu(CO)_2Cp)]$	6.21	114.2 <sup>c</sup>	213.2 <sup>c</sup>
$Cp_2ZrCl[(O_2CFe(CO)_2Cp)]$	6.08 <sup>c</sup>	114.2 <sup>c</sup>	206.2 <sup>c</sup>
$CpFe(CO)_2[C(O)OCH_3]$			213.3
$CpFe(CO)_2[C(O)OSi(CH_3)_3]$			213.8

<sup>a</sup> The chemical shifts are relative to TMS in  $CDCl_3$ . <sup>b</sup> The chemical shifts of the Cp ring on the Group IV metal. <sup>c</sup> In  $C_6D_6$ .

chemical shifts of Cp rings appear below  $\delta$  6.40 ppm from  $\delta$  6.39 ppm for complex **5** to  $\delta$  6.21 ppm for  $Cp_2ZrCl(O_2CR)$  ( $R = C(CH_3)_3$  or  $Ru(CO)_2Cp$ ). However the changes of the  $^{13}C$  chemical shifts of Cp rings for these zirconocene complexes are relatively small from  $\delta$  114.4 to 114.8 ppm. For the  $^{13}C$  chemical shifts of the carboxylate carbons, significant changes in terms of the R group in  $Cp_2MX(O_2CR)$  are worth noting. With the carboxylate carbon bonded directly to the transition metal, as in the complex  $CpFe(CO)_2[C(O)OCH_3]$  or  $CpFe(CO)_2[C(O)OSi(CH_3)_3]$ , the  $^{13}C$  chemical shift appears above 200 ppm. For the bimetallic zirconocene complexes  $Cp_2ZrCl[(O_2CM(CO)_2Cp)]$ , the  $^{13}C$  chemical shifts of the carboxylate carbon taken in  $C_6D_6$  solution are  $\delta$  213.2 ppm for  $M = Ru$  and  $\delta$  206.2 ppm for  $M = Fe$ . For R of the electron-donating group, such as  $CH_3$  or  $C(CH_3)_3$ , the  $^{13}C$  chemical shifts are around 190 ppm. For R of unsaturated hydrocarbons such as the aryl or vinyl group in  $[Cp_2TiOC(O)C_6H_4C(O)O]_4$  or  $[Cp_2TiOC(O)CH=CHC(O)O]_2$ , the  $^{13}C$  chemical shifts of the carboxylate carbons appear at  $\sim \delta$  170 ppm. For complexes **4**, **5**, and  $Cp_2M[(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$  ( $M = Ti$  or  $Zr$ ) in which the unsaturated aromatic phenyl or Cp rings are further complexed to a second metal, the  $^{13}C$  chemical shifts of the carboxylate carbons also appear at  $\sim \delta$  170 ppm. The upfield shift of  $^{13}C$  NMR of the carboxylate carbons bonded to the unsaturated  $sp^2$  or  $sp$  carbons is likely due to the delocalization of  $\pi$  electrons among the carboxylate and the unsaturated hydrocarbons. Further evidence of delocalization of the  $\pi$  electrons is given by the nearly planar geometry

of the carboxylate group and the unsaturated hydrocarbon. However, for the carboxylate carbons in complexes where the unsaturated hydrocarbon is further complexed to a second metal like complexes **3**, **5**, and others or without complexation to a second metal, the differences in the  $^{13}\text{C}$  chemical shifts are small.

For the  $(\text{O}_2\text{CC}_6\text{H}_5)_2\text{Cr}(\text{CO})_3$  moieties, the  $^{13}\text{C}$  chemical shifts of the carbonyl carbons at  $\sim 232.0$  ppm are rather insensitive to the early metal centers. The  $^1\text{H}$  NMR shows one signal for the corresponding *ortho*-, *meta*-, or *para*-protons of the monodentate and bidentate benzoate groups in complex **5**. Similarly, the  $^{13}\text{C}$  NMR also exhibits a single resonance for the corresponding carbons in the phenyl rings and for the carboxylate carbons. This result indicates a facile monodentate–bidentate carboxylate interconversion in solution (eqn. (3)) and this interconversion is a typical feature for the bis(carboxylato) complexes of zirconocene [17a,19].



### 3.2. The molecular structures of complexes **3** and **5**

The atomic coordinates and equivalent isotropic displacement coefficients of complexes **3** and **5** are listed in Tables 4 and 5 and the molecular structures are shown in Figs. 1 and 2. The selected bond lengths and bond angles for complexes **3** and **5** are listed in Table 6. The molecular structure of **3** shows a monodentate attachment of the carboxylate group to the small titanium metal. The monodentate carboxylate is a usual feature for the carboxylate complexes of titanocene due to the steric crowdedness around the small titanium metal center which prevents the bidentate coordination of carboxylate groups to achieve the saturated 18-electron configuration. The Ti–O bond distance (1.940(3) Å) is shorter than the distances in  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_2$  [25] (1.978(2) Å) and  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_4 \cdot \text{CH}_2\text{Cl}_2$  [25] (1.96(1) Å) but longer than that in  $\text{Cp}_2\text{Ti}[\text{OC}(\text{O})\text{C}_6\text{H}_5]_2$  [18b] (1.926 Å). The average Ti–Cp(centroid) distance in **3** (2.062 Å) is nearly identical to the distances in  $\text{Cp}_2\text{Ti}[\text{OC}(\text{O})\text{C}_6\text{H}_5]_2$  (2.061 Å) and  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_2$  (2.063 Å) but longer than the distance in  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_4 \cdot \text{CH}_2\text{Cl}_2$  (2.04 Å). The Ti–O–C(12) angle at 149.6(3)° is similar to the angle in  $\text{Cp}_2\text{Ti}[\text{OC}(\text{O})\text{C}_6\text{H}_5]_2$  at 148.2(6)°. However, this angle is substantially larger than those in  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_2$  (141.4°),  $[\text{Cp}_2\text{TiOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{O}]_4 \cdot \text{CH}_2\text{Cl}_2$  (140.5°), and other coordinatively saturated complexes that contain monodentate carboxylate ligands (114–137°) [26]. The rela-

TABLE 4. Atomic coordinates and equivalent isotropic displacement coefficients ( $\text{\AA}^2$ ) of complex **3**

Atom	x	y	z	$U_{\text{eq}}$
Ti	−0.3788(1)	0.9100(1)	0.7648(1)	0.040(1)
Cr	0.0203(1)	0.4583(1)	0.7447(1)	0.033(1)
O1	−0.1895(3)	0.8254(3)	0.6728(3)	0.053(1)
O2	−0.2050(4)	0.7906(3)	0.5160(3)	0.068(2)
O19	0.0542(5)	0.1670(3)	0.8260(5)	0.103(3)
O20	−0.1300(5)	0.4125(4)	1.0122(3)	0.077(2)
O21	−0.3418(4)	0.4539(4)	0.7382(3)	0.069(2)
C1	0.8016(8)	0.0833(5)	0.6660(6)	0.075(3)
C2	0.6792(10)	0.1039(6)	0.7656(7)	0.087(4)
C3	0.5201(9)	0.1268(5)	0.7444(8)	0.086(4)
C4	0.5325(11)	0.1267(6)	0.6337(9)	0.095(5)
C5	0.7184(10)	0.0987(6)	0.5814(6)	0.084(3)
C6	0.5027(8)	−0.2941(6)	0.8623(7)	0.081(4)
C7	0.4241(9)	−0.2297(7)	0.9402(7)	0.087(4)
C8	0.3254(7)	−0.1164(6)	0.8779(8)	0.082(4)
C9	0.3390(8)	−0.1110(7)	0.7635(9)	0.090(4)
C10	0.4498(7)	−0.2224(7)	0.7537(8)	0.081(4)
C11	−0.2500(11)	0.8351(10)	0.9170(7)	0.091(4)
C12	−0.1373(5)	0.7690(4)	0.5979(4)	0.042(2)
C13	0.0226(4)	0.6690(3)	0.6182(3)	0.036(2)
C14	0.0879(5)	0.5961(4)	0.5444(3)	0.040(2)
C15	0.2262(5)	0.4976(4)	0.5663(4)	0.046(2)
C16	0.3076(5)	0.4699(4)	0.6610(4)	0.046(1)
C17	0.2478(5)	0.5430(4)	0.7320(4)	0.044(2)
C18	0.1044(5)	0.6425(4)	0.7114(3)	0.038(2)
C19	0.0461(5)	0.2792(5)	0.7939(5)	0.059(2)
C20	−0.0714(5)	0.4290(4)	0.9096(4)	0.048(2)
C21	−0.2009(5)	0.4564(4)	0.7391(3)	0.043(2)

tively short Ti–O distance and large Ti–O–C angle is a result of better Ti–O  $\pi$ -bonding for achieving an effective 18-electron configuration for the formally 16-electron titanocene complexes. The Cp(centroid)–Ti–Cp(centroid) angle at 132.4° is normal compared with those values for the carboxylate complexes of titanocene (131.7–134.8°). The Ti–C bond length of **3** (2.183(9) Å) is somewhat shorter than the Ti–C(alkyl) distance in  $(\eta^5\text{-C}_9\text{H}_7)_2\text{Ti}(\text{CH}_3)_2$  [27] (2.21 Å) and  $(\text{Me-Cp})_2\text{Ti}(\text{CH}_2\text{OCH}_3)\text{Cl}$  [28] (2.216 Å) and it is also shorter than the Ti–C(aryl) distance in  $\text{Cp}_2\text{Ti}(\text{Ph})_2$  [29] (2.27 Å),  $\text{Cp}_2\text{Ti}[(p\text{-C}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3]\text{Cl}$  [30] (2.213 Å), and  $\text{Cp}_2\text{Ti}[(o\text{-C}_6\text{H}_4\text{F})\text{Cr}(\text{CO})_3]\text{Cl}$  [30] (2.217 Å). The Cr–Ph(centroid) distance (1.709 Å), the average Cr–C(carbonyl) distance (1.833 Å), and the average C–O distance (1.153 Å) are normal compared with those of (*p*-arene)Cr(CO)<sub>3</sub> [31] and  $\text{Cp}_2\text{Ti}[(\mu\text{-OCH}_2\text{-C}_6\text{H}_5)_2\text{Cr}(\text{CO})_3]\text{Cl}$  [12]. The average C–C bond distance in the phenyl ring in **3** (1.402 Å) is similar to those distances in  $\text{Cp}_2\text{Ti}[(p\text{-C}_6\text{H}_4\text{CH}_3)\text{Cr}(\text{CO})_3]$  (1.407 Å) and  $\text{Cp}_2\text{Ti}[(o\text{-C}_6\text{H}_4\text{F})\text{Cr}(\text{CO})_3]$  (1.398 Å) in which these two complexes are also Ti–Cr bimetallic complexes but bridged directly by the phenyl group without the mediation of carboxylate group. However,

TABLE 5. Atomic coordinates and equivalent isotropic displacement coefficients ( $\text{\AA}^2$ ) of complex 5

Atom	x	y	z	$U_{eq}$
Zr	0.2027(1)	0.4581(1)	0.3070(1)	0.030(1)
Cr1	-0.2146(1)	0.2227(1)	-0.0292(1)	0.038(1)
Cr2	-0.1756(1)	0.0128(1)	0.3348(1)	0.028(1)
O1	0.2325(3)	0.2797(2)	0.4811(2)	0.058(1)
O2	0.0840(3)	0.4708(2)	0.1719(1)	0.044(1)
O3	0.1042(3)	0.3558(2)	0.3871(1)	0.044(1)
O4	-0.0638(2)	0.3414(2)	0.2292(1)	0.043(1)
O18	-0.3593(4)	-0.0192(2)	-0.1522(2)	0.082(1)
O19	0.0739(3)	0.1329(2)	0.0507(2)	0.075(1)
O20	0.0492(5)	0.2814(3)	-0.1436(2)	0.097(2)
O28	-0.2063(4)	0.0061(3)	0.1491(2)	0.079(1)
O29	-0.3164(5)	-0.2510(2)	0.2780(3)	0.103(2)
O30	0.1881(3)	-0.0261(3)	0.3231(2)	0.083(1)
C1	0.3440(5)	0.2927(3)	0.2505(3)	0.069(2)
C2	0.4409(8)	0.3541(6)	0.3322(5)	0.080(3)
C3	0.5305(4)	0.4697(4)	0.3279(3)	0.073(2)
C4	0.4835(4)	0.4739(3)	0.2438(3)	0.064(1)
C5	0.3724(5)	0.3656(3)	0.1978(3)	0.066(1)
C6	0.0571(5)	0.5911(3)	0.4021(2)	0.058(1)
C7	0.2327(5)	0.6108(3)	0.4450(2)	0.061(1)
C8	0.3492(5)	0.6660(3)	0.4000(3)	0.059(1)
C9	0.2494(5)	0.6786(2)	0.3285(2)	0.056(1)
C10	0.0679(5)	0.6332(3)	0.3314(2)	0.056(1)
C11	-0.0538(3)	0.3895(2)	0.1684(2)	0.036(1)
C12	-0.2044(3)	0.3488(2)	0.0937(2)	0.037(1)
C13	-0.2059(5)	0.4092(3)	0.0302(2)	0.047(1)
C14	-0.3431(5)	0.3658(3)	-0.0428(2)	0.059(1)
C15	-0.4775(5)	0.2630(3)	-0.0522(2)	0.061(1)
C16	-0.4795(4)	0.2027(3)	0.0129(2)	0.050(1)
C17	-0.3449(3)	0.2443(3)	0.0857(2)	0.041(1)
C18	-0.3046(4)	0.0726(3)	-0.1065(2)	0.052(1)
C19	-0.0392(4)	0.1657(3)	0.0209(2)	0.048(1)
C20	-0.0544(5)	0.2607(3)	-0.1005(2)	0.060(1)
C21	0.1032(3)	0.2818(2)	0.4319(2)	0.037(1)
C22	-0.0764(3)	0.1943(2)	0.4221(1)	0.032(1)
C23	-0.2256(3)	0.1904(2)	0.3631(2)	0.034(1)
C24	-0.3913(3)	0.1051(2)	0.3534(2)	0.038(1)
C25	-0.4067(3)	0.0222(3)	0.4017(2)	0.041(1)
C26	-0.2574(3)	0.0274(3)	0.4631(2)	0.040(1)
C27	-0.0943(3)	0.1122(2)	0.4730(2)	0.036(1)
C28	-0.1944(4)	0.0098(3)	0.2203(2)	0.045(1)
C29	-0.2635(4)	-0.1485(3)	0.3000(2)	0.052(1)
C30	0.0494(3)	-0.0103(3)	0.3288(2)	0.045(1)

these average C–C distances in the phenyl ring are longer by 0.02–0.03  $\text{\AA}$  than that in  $\text{Cp}_2\text{Ti}[\text{OC}(\text{O})\text{C}_6\text{H}_5]_2$  (1.377  $\text{\AA}$ ) in which the phenyl ring is free from coordination to a second metal.

The molecular structure of **5** shows one monodentate and one bidentate carboxylate bonding and this type of carboxylate bonding is typical for the bis(carboxylato) complexes of zirconocene in order to achieve the saturated 18-electron configuration around the larger zirconium metal center. Although the monodentate bonding of both carboxylates to titanium metal is a general feature for the bis(carboxylato) complexes

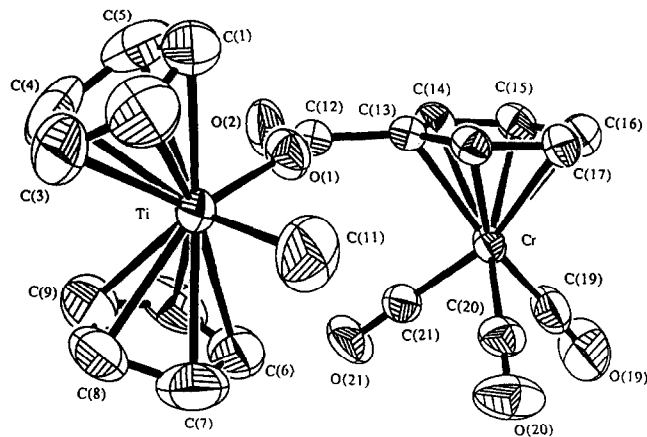


Fig. 1. The molecular structure of complex 3.

of Group IV metallocene, the electronically unsaturated 16-electron configuration of both monodentate carboxylates is not the case for the larger zirconium metal. The 20-electron configuration of both bidentate carboxylate bondings is also unfavourable electronically. The Zr–O bond distances of bidentate carboxylate ligands are inequivalent with the Zr–O(outer) distance longer (2.337(2)  $\text{\AA}$ ) than the Zr–O(inner) distance (2.250(2)  $\text{\AA}$ ). The Zr–O bond distance of the monodentate carboxylate ligand is substantially shorter at 2.085(2)  $\text{\AA}$ . The similar results of the Zr–O distances are also found in  $[\text{Cp}_2\text{Zr}(\text{O}_2\text{CC}=\text{CCO}_2)]_n$  [32] (Zr–O(outer), 2.332  $\text{\AA}$ ; Zr–O(inner), 2.261  $\text{\AA}$ ; Zr–O(monodentate), 2.113  $\text{\AA}$ ),  $[\text{Cp}_2\text{Zr}(\text{O}_2\text{CC}=\text{CCO}_2) \cdot \text{CHCl}_3]_n$  [32] (2.316  $\text{\AA}$ , 2.275  $\text{\AA}$ , 2.120  $\text{\AA}$ ), and  $[\text{Cp}_2\text{Zr}(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2)]_3 \cdot \text{CH}_2\text{Cl}_2$  [33] (2.33  $\text{\AA}$ , 2.24  $\text{\AA}$ , 2.07  $\text{\AA}$ ). The Zr–Cp(centroid) distance of **5** at 2.215  $\text{\AA}$  is in

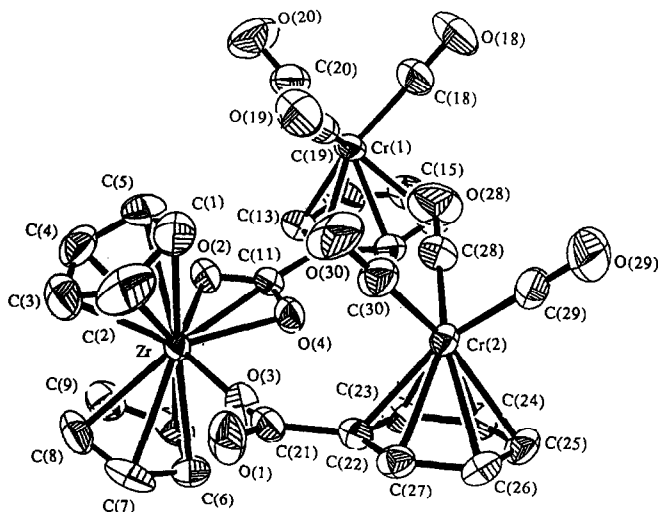


Fig. 2. The molecular structure of complex 5.

TABLE 6. Selected bond lengths (Å) and bond angles (°) of complexes 3 and 5

Complex 3			
Ti-O(1)	1.940(3)	Ti-C(11)	2.183(9)
O(1)-C(12)	1.281(6)	O(2)-C(12)	1.212(6)
C(12)-C(13)	1.508(5)	Ti-Cp(1)	2.060
Ti-Cp(2)	2.063	Cr-Ph	1.709
Ti-O(1)-C(12)	149.6(3)	O(1)-Ti-C(11)	92.1(3)
O(1)-C(12)-O(2)	125.4(4)	O(1)-C(12)-C(13)	114.3(4)
O(2)-C(12)-C(13)	120.3(4)	Cp(1)-Ti-Cp(2)	132.4
Cr-C(19)-O(19)	176.9(4)	Cr-C(20)-O(20)	179.0(4)
Cr-C(21)-O(21)	178.6(3)		
Complex 5			
Zr-O(2)	2.337(2)	Zr-O(3)	2.085(2)
Zr-O(4)	2.250(2)	O(1)-C(21)	1.219(3)
O(2)-C(11)	1.256(3)	O(3)-C(21)	1.276(4)
O(4)-C(11)	1.259(3)	C(11)-C(12)	1.486(3)
C(21)-C(22)	1.505(3)	Zr-Cp(1)	2.215
Zr-Cp(2)	2.215	Cr(1)-Ph(1)	1.702
Cr(2)-Ph(2)	1.708		
Zr-O(2)-C(11)	90.2(2)	Zr-O(3)-C(21)	156.6(2)
Zr-O(4)-C(11)	94.1(1)	O(1)-C(21)-O(3)	125.1(2)
O(1)-C(21)-C(22)	120.0(3)	O(2)-C(11)-O(4)	119.2(2)
O(2)-Zr-O(3)	133.0(1)	O(2)-C(11)-C(12)	121.2(2)
O(2)-Zr-O(4)	56.4(1)	O(3)-C(21)-C(22)	114.8(2)
O(4)-C(11)-C(12)	119.2(2)	Cp(1)-Zr-Cp(2)	129.6

the range of 2.204–2.220 Å for the above related zirconocene complexes. The O(outer)–Zr–O(monodentate) angle (133.0(1)°), the O(outer–Zr–O(inner)) angle (56.4(1)°) and the Cp(centroid)–Zr–Cp(centroid) angle (129.6°) are also comparable with those values in the bis(carboxylato) complexes of zirconocene such as [Cp<sub>2</sub>Zr(O<sub>2</sub>CC≡CCO<sub>2</sub>)<sub>n</sub>] (131.4°, 56.4°, 128.6°), [Cp<sub>2</sub>Zr(O<sub>2</sub>CC≡CCO<sub>2</sub>)·CHCl<sub>3</sub>]<sub>n</sub> (131.2°, 55.7°, 128.7°), or [Cp<sub>2</sub>Zr(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>] (132.9°, 56.7°, 130.1°). However, the Zr–O–C angles of the monodentate carboxylate ligand, 154.3(6)° for [Cp<sub>2</sub>Zr(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>] and 156.6(2)° for complex 5, are substantially larger than those angles for [Cp<sub>2</sub>Zr(O<sub>2</sub>C≡CCO<sub>2</sub>)<sub>n</sub>] (141.3°) and [Cp<sub>2</sub>Zr(O<sub>2</sub>CC≡CCO<sub>2</sub>)·CHCl<sub>3</sub>]<sub>n</sub> (144.3°). In the former two complexes, the large Zr–O–C angles and short Zr–O distances are the result of stronger Zr–O π-interaction. For the (O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub> moieties in 5, all atoms in the two O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub> groups are nearly in a plane which bisects the Cp(centroid)–Zr–Cp(centroid) plane. Both Cr metals are on the same side of the plane with an average Cr–Ph(centroid) distance of 1.705 Å. The average C–C bond distances of the phenyl ring attached to the monodentate and bidentate carboxylate groups are very similar at 1.409 and 1.404 Å, respectively. In complex 3 containing monodentate carboxylate, the value is 1.409 Å. The average M–C(carbonyl) bond distances for the following complexes are in the order of complex 5

(1.844 Å) > complex 3 (1.833 Å) ~ Cp<sub>2</sub>Zr[(μ-OCH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>]<sub>2</sub> (1.832 Å) > Cp<sub>2</sub>TiCl[(o-C<sub>6</sub>H<sub>4</sub>F)Cr(CO)<sub>3</sub>] (1.812 Å) > Cp<sub>2</sub>TiCl[(p-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cr(CO)<sub>3</sub>] (1.804 Å) and the average C–O bond distances for these complexes are in reverse order. This trend reflects the π-bonding abilities of chromium metal to carbonyls. However, further investigation of these types of bimetallic complexes are needed to understand fully the effect of these bridging arene systems on the π-bonding abilities of the Cr metal center.

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