

The synthesis and characterization of Group 4 metal–chromium complexes bridged by an $\text{OCH}_2\text{C}_5\text{H}_4$ group

The molecular structure of $\text{Cp}_2\text{TiCl}[(\text{OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]$

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Abstract

The series of complexes $\text{Cp}_2\text{TiY}[(\mu\text{-OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]$ ($\text{Y} = \text{Cl}$ (1), Br (2), or CH_3 (3)) and $\text{Cp}_2\text{ZrY}[(\mu\text{-OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]$ ($\text{Y} = \text{CH}_2\text{Ph}$ (4) or $(\mu\text{-OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ (5)) were prepared from the reactions of $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ with suitable Group 4 metallocene derivatives. The IR spectra of complexes 1–5 show that the $\nu(\text{CO})$ and $\nu(\text{NO})$ shift to lower frequencies relative to the values for $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$. This observation indicates more π -backbonding from the chromium metal center to the two CO and the NO ligands upon complexation of $(\text{OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ to the early metal. The complex 1 crystallizes in the monoclinic $P2_1/n$ space group with cell parameters $a = 11.274(2) \text{ \AA}$, $b = 13.135(3) \text{ \AA}$, $c = 13.091(3) \text{ \AA}$, $\beta = 105.46(3)^\circ$, $z = 4$, $R = 0.045$, $R_w = 0.054$ and $\text{Gof} = 1.23$. The slightly long C–O and N–O distances, the considerably weak Ti–O bond and the upfield shift of the ^1H and ^{13}C chemical shifts of C_5H_4 group also support the argument of net electron flow from OCH_2 group to C_5H_4 group in which the cumulated electron density would pass to the chromium metal center and then π -backbonding to the CO and NO ligands for the observation of lower energies of $\nu(\text{CO})$ and $\nu(\text{NO})$ bands. © 1997 Elsevier Science S.A.

Keywords: Metal–chromium complexes; Bimetallic complexes

1. Introduction

The chemistry of early–late bimetallic complexes have attracted considerable attention in the past 15 years and the main purpose of these studies is to synthesize complexes which have a cooperative effect of both the early and late metals in catalytical reactions [1]. Among the bridging ligands in the early–late bimetallic complexes [2], ring-substituted aryl ligands are an important and interesting type of ligand for the preparation of bimetallic complexes containing the $(\text{arene})\text{Cr}(\text{CO})_3$ moiety for two reasons. First, the easy availability of diversified ring-substituted $(\text{arene})\text{Cr}(\text{CO})_3$ complexes as metalloligands. Second, the comprehensive structural data, including the geometric orientation of the $\text{Cr}(\text{CO})_3$ tripod [3], the structural distortion from the planarity of

the arene ring [4], and the electronic effect caused by the variations of the ring-substituent [5], are available for comparison. In these studies, several series of Group 4–chromium bimetallic complexes of $\text{Cp}_2\text{MY}[(\mu\text{-XC}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3]$ ($\text{M} = \text{Ti}$ or Zr ; $\text{Y} = \text{alkyl}$, alkoxide , or halide ; $\text{X} = \text{O}$, OCH_2 , or O_2C) were reported by Heppert et al. [6] and by us [7,8]. However, besides the structural effects on the $(\text{arene})\text{Cr}(\text{CO})_3$ moiety and the upfield shift of the ^1H and ^{13}C chemical shifts of the arene ring, little effect was observed on the electronic state of the CO ligands upon the change of the Y ligands on the early metal center. These results prompt us to shift our study to a bimetallic complex system bridging through the ring-substituted Cp ligand and here we report the reactions of Group 4 metallocenes with $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ which contains a hydroxymethyl group on the cyclopentadienyl ring and a strong labilizing and probably better π -accepting NO ligand on the chromium metal center. In this study, the

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series of complexes $Cp_2TiY[(\mu-OCH_2C_5H_4)Cr(CO)_2(NO)]$ ($Y = Cl$ (1), Br (2), or CH_3 (3)) and $Cp_2ZrY[(\mu-OCH_2C_5H_4)Cr(CO)_2(NO)]$ ($Y = CH_2Ph$ (4) or $(OCH_2C_5H_4)Cr(CO)_2(NO)$ (5)) were prepared. The IR spectra of these complexes show that the $\nu(CO)$ and $\nu(NO)$ peaks shift to lower frequencies relative to the values for $(HOCH_2C_5H_4)Cr(CO)_2(NO)$. This observation indicates more backbonding from the chromium metal center to the two CO and the NO ligands upon complexation of $(OCH_2C_5H_4)Cr(CO)_2(NO)$ to the early metal center.

2. Experimental sections

2.1. Reagents and general techniques

$(HOCH_2C_5H_4)Cr(NO)(CO)_2$ is prepared in a modified literature procedure [9] with the addition of 5 ml of 1% aqueous HCl solution instead of 15 ml of 10% aqueous HCl solution in the final step of the procedure. $Cp_2Ti(CH_3)_2$ [10], $Cp_2Zr(CH_2C_6H_5)_2$ [11], and $Cp_2Zr(CH_3)_2$ [12] were prepared according to the literature procedures. Cp_2TiBr_2 was prepared by reaction of Cp_2TiCl_2 with BBr_3 . Cp_2TiCl_2 (Aldrich) was used without further purification. NEt_3 (Merck) was distilled over KOH pellets and stored over molecular sieves. Solvents were dried by refluxing at least 24 h over P_2O_5 (dichloromethane) or sodium–benzophenone (benzene, hexane, diethyl ether) 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 $Cp_2TiCl[(\mu-OCH_2C_5H_4)Cr(NO)(CO)_2]$ (1)

To a flask containing Cp_2TiCl_2 (1.50 g, 6.00 mmol) and $(HOCH_2C_5H_4)Cr(NO)(CO)_2$ (1.40 g, 6.00 mmol) in 30 ml of benzene, NEt_3 (0.90 ml, 6.00 mmol) was added slowly. The reaction mixture was stirred at room temperature for 20 h and was filtered. The solvent was removed and the residue was dissolved in 100 ml of diethyl ether. The solution was concentrated to 80 ml and was allowed to stand at $-15^\circ C$ for 48 h to afford red crystals (1.58 g, 59.1%), m.p. $98.1-99.8^\circ C$. Anal. Found: C, 48.46; H, 3.71; N, 3.47. $C_{18}H_{16}ClCrNO_4Ti$ calc.: C, 48.51; H, 3.62; N, 3.14%.

2.3. Synthesis of $Cp_2TiBr[(\mu-OCH_2C_5H_4)Cr(NO)(CO)_2]$ (2)

To a solution of Cp_2TiBr_2 (0.357 g, 1.06 mmol) and $(HOCH_2C_5H_4)Cr(NO)(CO)_2$ (0.247 g, 1.06 mmol) in 30 ml of benzene at room temperature, NEt_3 (0.15 ml,

1.10 mmol) was syringed-in slowly and the mixture was stirred for 22 h. The resulting solution was filtered and dried in vacuo. The residue was dissolved in 80 ml of diethyl ether and the solution was concentrated to 40 ml and then allowed to stand at $-15^\circ C$ for 48 h to give an orange solid (0.565 g, 53.5%), m.p. $109.8-111.0^\circ C$. Anal. Found: C, 44.04; H, 3.48; N, 3.12. $C_{18}H_{16}BrCrNO_4Ti$ calc.: C, 44.11; H, 3.29; N, 2.86%.

2.4. Synthesis of $Cp_2Ti(CH_3)[(\mu-OCH_2C_5H_4)Cr(NO)(CO)_2]$ (3)

To a flask shielded from the light which contained $Cp_2Ti(CH_3)_2$ (0.467 g, 2.24 mmol) and $(HOCH_2C_5H_4)Cr(NO)(CO)_2$ (0.540 g, 2.32 mmol), 30 ml of dichloromethane was added and the mixture was stirred at $0^\circ C$ for 16 h. The solvent was removed and the orange residue was dissolved in 80 ml of hexane. The solution then was concentrated to 60 ml and allowed to stand at $-15^\circ C$ for 24 h to afford orange crystals (0.667 g, 70.0%), m.p. $66.5-67.9^\circ C$. Anal. Found: C, 53.12; H, 4.49; N, 3.80. $C_{19}H_{19}CrNO_4Ti$ calc.: C, 53.66; H, 4.50; N, 3.29%.

2.5. Synthesis of $Cp_2Zr(CH_2C_6H_5)[(\mu-OCH_2C_5H_4)Cr(NO)(CO)_2]$ (4)

A mixture of $Cp_2Zr(CH_2Ph)_2$ (0.573 g, 1.42 mmol) and $(HOCH_2C_5H_4)Cr(NO)(CO)_2$ (0.331 g, 1.42 mmol) in 30 ml of benzene was reacted at room temperature for 4 h and then the solvent was removed. The residue was dissolved in 60 ml of diethyl ether and then the solution was concentrated to 40 ml. Red crystals (0.621 g, 80.3%), m.p. $111.3-112.4^\circ C$, were obtained after the solution was left standing at $-15^\circ C$ for 72 h. Anal. Found: C, 55.13; H, 4.37; N, 2.83. $C_{25}H_{23}CrNO_4Zr$ calc.: C, 55.13; H, 4.26; N, 2.57%.

2.6. Synthesis of $Cp_2Zr[(\mu-OCH_2C_5H_4)Cr(NO)(CO)_2]_2$ (5)

To a flask containing $Cp_2Zr(CH_3)_2$ (0.20 g, 0.80 mmol) and $(HOCH_2C_5H_4)Cr(NO)(CO)_2$ (0.373 g, 1.60 mmol), a mixture of diethyl ether/hexane solvents (2/1; 50 ml) was added at room temperature. The resulting solution was reacted for 4 h and then was cooled at $-15^\circ C$ for 72 h to afford red crystals (0.42 g, 76.6%), m.p. $114.3-115.1^\circ C$. Anal. Found: C, 46.18; H, 3.63; N, 4.39. $C_{26}H_{22}Cr_2N_2O_8Zr$ calc.: C, 45.54; H, 3.23; N, 4.09%.

2.7. Physical measurements

1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz)

Table 1
Crystallographic data of $\text{Cp}_2\text{TiCl}[(\text{OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{NO})(\text{CO})_2]$ (1)

Formula	$\text{C}_{18}\text{H}_{16}\text{NO}_4\text{ClTiCr}$
Formula weight	445.7
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.274(2)
b (Å)	13.135(3)
c (Å)	13.091(3)
β (deg)	105.46(3)
V (Å ³)	1868.4(11)
z	4
D_{calc} (g cm ⁻³)	1.584
$\lambda(\text{Mo K}\alpha)$ (Å)	0.71073
Absorption coefficient (mm ⁻¹)	1.174
Range (deg)	3.0–45
Scan type	$\theta-2\theta$
Number of reflections collected	2699
Number of independent reflections	2419 ($R_{\text{int}} = 3.93\%$)
Number of observed reflections	1693 ($I > 2\sigma I$)
No. of refined parameter	235
R^a for significant reflections	0.045
R_w^b for significant reflections	0.054
Goodness of fit ^c	1.23

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

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

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

spectrometer and ¹³C NMR spectra were recorded with the Varian VXR-300 (75.43 MHz) spectrometer. The ¹H and ¹³C chemical shifts were measured relative to tetramethylsilane as the internal reference. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument. 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. Melting points were measured under a dry dinitrogen atmosphere using a Büchi 535 instrument and were not corrected.

2.8. Crystal structure determinations

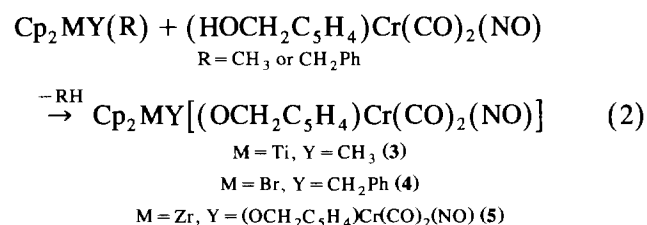
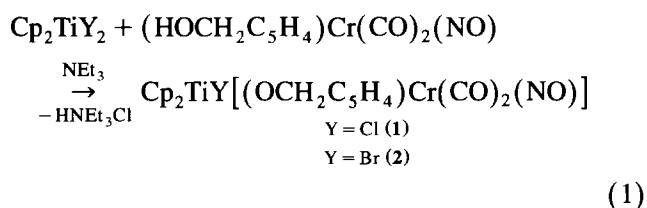
An orange crystal of **1** of size 0.40 × 0.60 × 0.70 mm³ in a sealed capillary under dinitrogen atmosphere was used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). 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 the 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 Å 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 the complex **1** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The bimetallic complexes **1–5** were prepared by the reactions of titanocene dihalides in the presence of NEt_3 or by the de-alkylation reactions of Group 4 metallocene derivatives with $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ (Eqs. (1) and (2)). These complexes are quite soluble in ether and the complex **3** is even soluble in hexane. Though complexes **1–5** can be stored under dry dinitrogen atmosphere for weeks, they decompose rapidly when exposed to air.



The IR spectral data for $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ complexes **1–5** in Nujol mull, and other related com-

Table 2
The IR spectra of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})\text{Cr}(\text{CO})_2(\text{NO})$, complexes **1–5**, and related complexes

Complex	$\nu(\text{CO})$	$\nu(\text{NO})$	Reference
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})\text{Cr}(\text{CO})_2(\text{NO})$	2032 (s), 1956 (s)	1710 (s)	This work ^a
1	2020 (s), 1932 (s)	1686 (s)	This work ^b
2	2014 (s), 1947 (s)	1668 (s)	This work ^b
3	2020 (s), 1959 (s)	1710 (s)	This work ^b
4	2008 (s), 1926 (s)	1684 (s)	This work ^b
5	2020 (s), 1944 (s)	1698 (s)	This work ^b
$\text{CpCr}(\text{CO})_2(\text{NO})$	2028, 1959	1719	[13] ^c
$\text{Cp}^*\text{Cr}(\text{CO})_2(\text{NO})$	2000 (s), 1930 (s)	1675 (s)	[14] ^d

^a Neat substance. The IR bands reported by Macomber and Rausch are at 1675 (s) for $\nu(\text{NO})$ and 2000 (s) and 1930 (s) for $\nu(\text{CO})$ [9].

^b Nujol mull.

^c In pentane.

^d In CH_2Cl_2 .

Table 3

¹H NMR data of (HOCH₂C₅H₄)Cr(NO)(CO)₂ and complexes 1–5, Cp₂MY[(OCH₂C₅H₄)Cr(NO)(CO)₂]^a

Complex	Cp	C ₅ H ₄	CH ₂ O	CH ₃	CH ₂ Ph	C ₆ H ₅
(HOCH ₂ C ₅ H ₄)Cr(NO)(CO) ₂ ^b	—	5.17(t,2H) 5.00(t,2H)	4.35(d,2H)			
1, M = Ti, Y = Cl	6.34(s,10H)	5.04(t,2H) 4.95(t,2H)	5.07(s,2H)			
2, M = Ti, Y = Br	6.38(s,10H)	5.03(t,2H) 4.95(t,2H)	5.03(s,2H)			
3, M = Ti, Y = CH ₃	5.95(s,10H)	4.94(t,2H) 4.91(t,2H)	4.72(s,2H)	0.55(s,3H)		
4, M = Zr, Y = CH ₂ C ₆ H ₅	5.95(s,10H)	5.01(t,2H) 4.99(t,2H)	4.56(s,2H)		2.30(s,2H)	7.16(m,3H) 6.83(m,2H)
5, M = Zr, Y = (OCH ₂ C ₅ H ₄)Cr(NO)(CO) ₂ C ₅ H ₄)Cr(NO)(CO) ₂ (HOCH ₂ C ₅ H ₄)Cr(NO)(CO) ₂ ^c	6.23(s,10H)	5.04(t,4H) 4.99(t,4H)	4.64(s,4H)			
		5.17(t,2H) 4.98(t,2H)	4.33(s,2H)			

^a CDCl₃ solution with TMS as the internal standard.^b The ¹H resonance of –OH appears at 1.57 (t) ppm.^c Ref. [9]; OH peak is at 2.05 (s) ppm.

plexes [9,13,14] in the CO and NO region are listed in Table 2. The CO and NO stretching frequencies in this study are, in general, sensitive to the electronic state of metal centers and to the donating ability of other ligands on the metal. For Cp*Cr(CO)₂(NO) [14], the ν(CO) and ν(NO) bands are about 30 and 50 cm⁻¹ lower than that for CpCr(CO)₂(NO) [13], indicating a better electron-donating ability of the Cp* ligand. The similar ν(CO) and ν(NO) frequencies for (HOCH₂C₅H₄)Cr(CO)₂(NO) relative to the frequencies for CpCr(CO)₂(NO) suggest that the cyclopentadienyl

ring-substituted hydroxymethyl group has little effect on the electronic state of the Cr metal center. However, after complexation of (HOCH₂C₅H₄)Cr(CO)₂(NO) to the Group 4 metallocene, the ν(CO) bands shift to lower energies by about 10–20 cm⁻¹ and the ν(NO) frequencies, except 3 which has a similar ν(NO) value to the frequency for the (HOCH₂C₅H₄)Cr(CO)₂(NO) shift, also shift to lower energies by about 10 to 40 cm⁻¹. The observations of lower frequencies of the CO and NO bands indicate more π-backbonding to both the CO and NO ligands after the formation of bimetallic com-

Table 4

¹³C NMR data of (HOCH₂C₅H₄)Cr(NO)(CO)₂ and complexes 1–5^a

Complex	Cp	C ₅ H ₄	CH ₂ O	CO	CH ₃ or CH ₂ Ph	C ₆ H ₅
(HOCH ₂ C ₅ H ₄)Cr(NO)(CO) ₂	—	112.4 89.5 89.3	58.5	236.8		
1, M = Ti, Y = Cl	116.9	115.4 88.9 88.2	76.3	237.8		
2, M = Ti, Y = Br	117.0	115.5 89.2 88.5	78.0	238.3		
3, M = Ti, Y = CH ₃	112.2	116.7 88.7 87.7	72.5	237.7	34.5	
4, M = Zr, Y = CH ₂ C ₆ H ₅ ^b	111.5	112.1 89.4 88.0	68.7	238.4	47.6	153.5 128.2 126.9 120.9
5, M = Zr, Y = (OCH ₂ C ₅ H ₄)Cr(NO)(CO) ₂	112.1	113.9 89.1 88.0	68.6	237.7		

^a In CDCl₃ solution.^b In C₆D₆ solution.

Table 5

Atomic coordinates and equivalent isotropic displacement coefficients (\AA^2) of the complex 1

Atom	x	y	z	U_{eq}
Cr	0.1806(1)	0.8562(1)	0.6314(1)	0.050(1)
Ti	-0.1677(1)	0.6100(1)	0.6967(1)	0.038(1)
Cl	-0.1223(2)	0.4328(1)	0.6879(2)	0.077(1)
O(1)	-0.0129(3)	0.6472(3)	0.6889(3)	0.050(2)
C(1)	-0.3167(7)	0.7204(6)	0.5927(6)	0.075(3)
C(2)	-0.3781(6)	0.6287(6)	0.5944(5)	0.066(3)
C(3)	-0.3284(7)	0.5561(7)	0.5450(6)	0.075(3)
C(4)	-0.2363(7)	0.6021(7)	0.5067(5)	0.080(4)
C(5)	-0.2310(7)	0.7036(7)	0.5361(6)	0.077(4)
C(6)	-0.0649(7)	0.6612(8)	0.8745(5)	0.077(4)
C(7)	-0.1625(9)	0.7259(6)	0.8357(6)	0.080(4)
C(8)	-0.2698(7)	0.6683(8)	0.8220(6)	0.080(4)
C(9)	-0.2370(9)	0.5698(7)	0.8478(6)	0.081(4)
C(10)	-0.1097(9)	0.5659(8)	0.8815(6)	0.085(4)
C(11)	0.0624(6)	0.6253(5)	0.6220(5)	0.059(3)
C(12)	0.1762(5)	0.6889(5)	0.6494(5)	0.047(2)
C(13)	0.2483(6)	0.7143(5)	0.5780(6)	0.057(3)
C(14)	0.3488(6)	0.7724(5)	0.6354(7)	0.067(3)
C(15)	0.3417(6)	0.7848(6)	0.7397(6)	0.066(3)
C(16)	0.2347(6)	0.7325(5)	0.7483(5)	0.055(2)
N(17)	0.0595(5)	0.8670(4)	0.5179(5)	0.065(3)
O(17)	-0.0210(5)	0.8707(4)	0.4379(4)	0.092(2)
C(18)	0.2499(6)	0.9752(5)	0.6083(5)	0.054(3)
O(18)	0.2926(5)	1.0495(4)	0.5858(5)	0.087(3)
C(19)	0.0948(7)	0.9161(7)	0.7152(6)	0.080(3)
O(19)	0.0387(7)	0.9519(6)	0.7664(5)	0.145(4)

plexes. In the $\text{Cp}_2\text{TiCl}[(\mu\text{-C}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3]$ system reported by Lotz and coworkers [15] with the aryl carbon coordinated directly to the titanium metal center, the $\nu(\text{CO})$ bands are also observed to shift to lower energies by 15–21 cm^{-1} . They attributed this observation in

terms of the high basicity of the $(\text{C}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3$ moiety and the high Lewis acidity of the Ti(IV) metal center in which the transfer of electron density is likely via a donor/acceptor type of interaction or electrostatic attraction. In $\text{Cp}_2\text{MY}[(\mu\text{-XC}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3]$ systems [7,8], the $\nu(\text{CO})$ bands taken as Nujol mull are also observed to shift to lower energies. However, upon the change of the ligand Y on the early-transition metal center, the variations of $\nu(\text{CO})$ frequencies in $\text{Cp}_2\text{MY}[(\mu\text{-XC}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3]$ systems are observed to be small (in general less than 10cm^{-1}). In the present system of $\text{Cp}_2\text{TiY}[(\mu\text{-OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]$, the shifts of the $\nu(\text{NO})$ band are significantly larger ($\sim 40\text{cm}^{-1}$) upon change of the Y ligands and this enhanced effect may be attributed to the better π -acceptor characteristics of the NO ligand.

The ^1H and ^{13}C NMR spectra for $(\text{HOCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ and complexes 1–5 are listed in Tables 3 and 4. Based on the ^1H and ^{13}C chemical shifts of Cp groups attached to the Group 4 metal, the general trend for the donation abilities of the Y substituent in $\text{Cp}_2\text{MY}[(\mu\text{-OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]$ is in the order of $\text{Y} = \text{Alkyl} > (\text{OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO}) > \text{Cl} > \text{Br}$. This order is consistent with the results obtained from the complex systems of $\text{Cp}_2\text{MY}[(\mu\text{-XC}_6\text{H}_4\text{R})\text{Cr}(\text{CO})_3]$ [7,8]. For the $(\text{OCH}_2\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ moiety, the ^1H chemical shifts of C_5H_4 group are found to shift upfield. For the ^{13}C chemical shifts of the C_5H_4 group, except the ^{13}C chemical shifts of the substituted carbon which shifts downfield, also shift upfield slightly. The similar upfield shifts of ^1H and ^{13}C resonances are also observed in complex systems bridged by the substituted aryl groups, indicating an increasing electron density on the

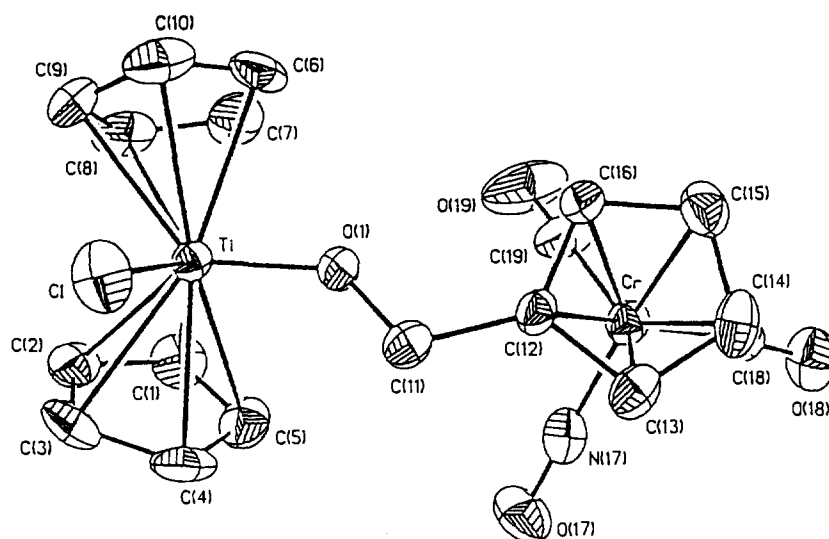


Fig. 1. Molecular structure of 1.

Table 6
The selected bond distances (Å) and bond angles (deg) for complex **1**^a

Ti–O(1)	1.841(4)	Ti–Cl	2.392(2)
O(1)–C(11)	1.403(8)	C(11)–C(12)	1.492(8)
Ti–Cp(1)	2.080	Ti–Cp(2)	2.073
Cr–N(17)	1.735(6)	N(17)–O(17)	1.190(7)
Cr–C(18)	1.809(7)	C(19)–O(19)	1.161(9)
Cr–C(19)	1.824(9)	C(19)–O(19)	1.139(12)
Cr–Cp(3)	1.841	[Cr–C(Cp)] _{ave}	2.197
Cl–Ti–O(1)	92.1(1)	Ti–O(1)–C(11)	136.1(3)
Cp(1)–Ti–Cp(2)	130.8	O(1)–C(11)–C(12)	111.1(5)
Cr–N(17)–O(17)	176.7(6)	Cr–C(18)–O(18)	175.0(6)
Cr–C(19)–O(19)	178.2(7)		

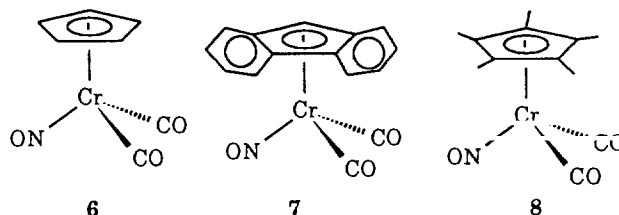
^a Cp(1) = C(1)–C(5); Cp(2) = C(6)–C(10); Cp(3) = C(12)–C(16).

arene ligand [7,8]. In contrast to the upfield shift of the C₅H₄ ring, the ¹H and ¹³C chemical resonances for the OCH₂ group shift downfield substantially. The upfield shift of the C₅H₄ group and the downfield shift of OCH₂ consistently indicate an electron-withdrawing from the OCH₂ group by the C₅H₄ group. This observation is in parallel to the result suggested by the IR data, since the electron density cumulated on the C₅H₄ ring would pass to the chromium metal center and then π -backbonding to the CO and NO ligands for the observation of lower energy bands of ν (CO) and ν (NO).

3.2. The molecular structure of **1**

The atomic coordinates and equivalent isotropic displacement coefficient of **1** are listed in Table 5 and the molecular structure is shown in Fig. 1. The selected bond lengths and bond angles for **1** are listed in Table 6. The Ti–O(1) distance at 1.841(4) Å is considerably longer than typical Ti–OR distances in titanocene alkoxide complexes [7,16]. In parallel with the long Ti–O distance, the Ti–O(1)–C(11) angle at 136.1(3)° is relatively small, indicating negligible Ti–O π bonding in **1**. Similarly, the Ti–Cl distance at 2.392(2) Å is slightly longer than the distances in titanocene dichlorides [17]. In **1**, the N(17)–O(17) distance and the two C–O distances are 1.190(7) Å, and 1.161(9) and 1.139(12) Å respectively. These distances are slightly longer than the N–O and the C–O distances in complex **7** at 1.169(9) and 1.145(6) Å [9]. For complexes **6** [13] and **8** [14], disorders are found for the CO and NO ligands which prevent a direct comparison with our results. However, the average X–O (X = C or N) distance at 1.163 Å for **1** is also slightly longer than the average X–O distances of 1.159 Å for **6** and of 1.154 Å for **8**. The observation of the comparably weak Ti–O bond seems in parallel to the argument of the net flow of electron density from OCH₂ to the C₅H₄ ring and

then π -backbonding to the CO and NO ligands to give slightly long C–O and N–O distances.



4. Conclusion

A facile way for the preparation of Group 4–chromium bimetallic complexes of formula Cp₂MY[(μ -OCH₂C₅H₄)Cr(CO)₂(NO)] is demonstrated. The IR spectra of these complexes show more π -backbonding from the chromium metal to the CO and NO ligands, indicating a net electron-withdrawing from the OCH₂ group to the (C₅H₄)Cr(CO)₂(NO) moiety; this is probably due to the better π -acceptor ability of the NO ligand. The downfield shift of the ¹H and ¹³C chemical shifts of the OCH₂ group and the relatively weak Ti–O bond in complex **1** also support the argument.

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