

Syntheses and spectra of chromium–titanium complexes bridged by carboxylate substituted cyclopentadienyl group: The structure of $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{NO})_2\text{Cl}\}$

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Abstract

Mono-demethylation of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ in dichloromethane with 1 M equivalent of $[\eta^5\text{-(C}_5\text{H}_4\text{COOH)]Cr}(\text{CO})_2\text{NO}$ (**5**), $[\eta^5\text{-(C}_5\text{H}_4\text{COOH)]Cr}(\text{NO})_2\text{X}$ ($\text{X} = \text{Cl}$ **6**, $\text{X} = \text{I}$ **7**) and $[\eta^5\text{-(C}_5\text{H}_4\text{COOH)]W}(\text{CO})_3\text{CH}_3$ (**8**) gives $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2\text{NO}\}$ (**9**), $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{NO})_2\text{Cl}\}$ (**10**), $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{NO})_2\text{I}\}$ (**11**) and $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{W}(\text{CO})_3\text{CH}_3\}$ (**12**), respectively. The structure of **10** has been solved by X-ray diffraction studies. One of the nitrosyl groups is located at the site away from the exocyclic carbonyl carbon of the Cp(Cr) ring with twist angle of 178.1°. All the data reveals that $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{-}$ is a strong electron-donating group. The opposite correlation was observed on the chemical shift assignments of C(2)–C(5) in compounds **5–12**, using HetCOR NMR spectroscopy, as compared with the NMR data of their ferrocene analogues. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data and those of **10** are compared with the calculations via density functional B3LYP correlation-exchange method.

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Keywords: Chromium; Titanium; Nitrosyl; ^{13}C NMR, B3LYP

1. Introduction

Albeit the chemistry of metallocenes of iron have been thoroughly explored, the number of isolated and well characterized Cp-functionally-substituted chlorochromium, iodochromium and methyltungsten complexes are relatively small. In the case of $\text{CpCr}(\text{NO})_2\text{Cl}$ (**2**), only two complexes, $(\text{Cp-COOCH}_3)\text{Cr}(\text{NO})_2\text{Cl}$ [**1**] and $[\text{Fc-C}(\text{O})\text{-Cp}]\text{Cr}(\text{NO})_2\text{Cl}$ [**2**], are reported in the literature. For the analogue of $\text{CpCr}(\text{NO})_2\text{I}$ (**3**) there is only one, $(\text{Cp-COOCH}_3)\text{Cr}(\text{NO})_2\text{I}$, and for complex $\text{CpW}(\text{CO})_3\text{CH}_3$ (**4**) there are 17 [**3**].

The Cp–chromium complexes may have properties distinct from their iron analogues. Earlier [**4**], we reported the unequivocal assignments of C(2,5) and C(3,4) on the Cp ring of the (cyclopentadienyl)dicarbonylnitrosylchromium (hereafter called cynichrodene) **1** derivatives bearing electron-withdrawing substituent in ^{13}C NMR spectra. The opposite correlation on the assignments between ferrocene and cynichrodene **1** was a surprising finding. In the case of ferrocene [**5**], 3,4-positions are more sensitive to the electron-withdrawing substituent, while in the case of cynichrodene, the 2,5-positions are more sensitive to the electron-withdrawing substituent. The overall electron-withdrawing property of CO and NO ligands may exert the difference. The qualitative relationship of non-planarity of Cp-exocyclic carbon to substituent π -donor and π -acceptor interactions have also been addressed. The

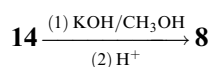
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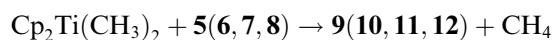
π -donor substituents and the *ipso*-carbon atoms to which they are attached are bent away from the $\text{Cr}(\text{CO})_2\text{NO}$ fragments while the π -acceptor substituents and the *ipso*-carbon atoms to which they are attached are approximately in the Cp plane or are bent slightly toward the $\text{Cr}(\text{CO})_2\text{NO}$ fragments. The magnitudes and directions of these distortions of the Cp planarity appear to be due primarily to electronic effects [4]. In hope of confirming those hypotheses, some Cp-functionally substituted metallocenes, containing $(\text{CO})_2\text{NO}$, $(\text{NO})_2\text{Cl}$, $(\text{NO})_2\text{Br}$, $(\text{NO})_2\text{I}$, $(\text{NO})_2(\text{N}=\text{C}=\text{S})$ and $(\text{NO})_2(\text{N}=\text{C}=\text{Se})$ were studied [1,4c].

Herein, we report thorough spectral studies on **5–12**, and the crystal structure of $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{Cl}\}$ (**10**). Complexes **10** and **11** appears to be the first example of a Cp-functionally substituted derivative of $\text{CpCr}(\text{NO})_2\text{Cl}$ and $\text{CpCr}(\text{NO})_2\text{I}$ containing early metal titanium, respectively. Through complex **10**, the strong electron-donating property of $\text{Cp}_2\text{Ti}(\text{CH}_3)-$ was prominently revealed.

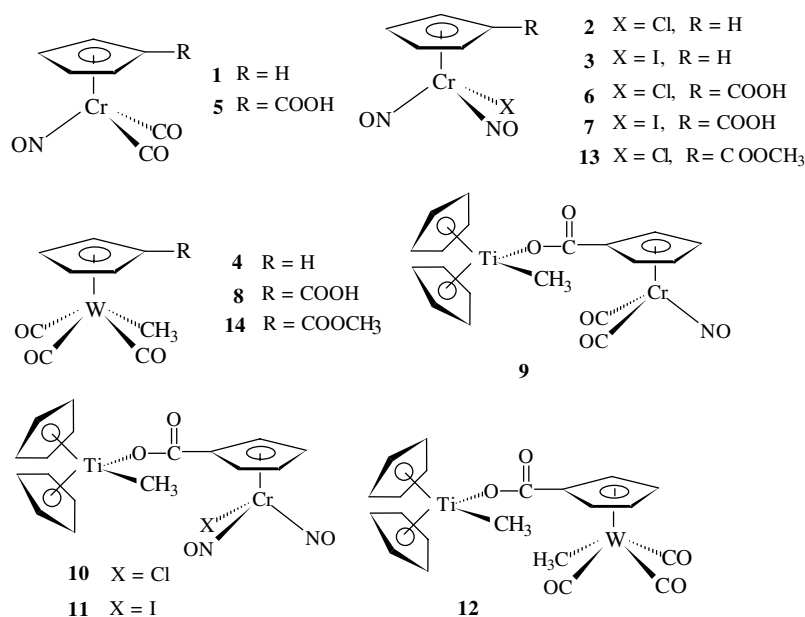
Complex $[\eta^5\text{-(C}_5\text{H}_4\text{-COOCH}_3\text{)]W}(\text{CO})_3\text{CH}_3$ (**14**) [6] was saponified under mild conditions with potassium hydroxide in aqueous methanol at 25 °C to give the corresponding carboxylic acid **8** in 79% yield.



Complexes, $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{CO})_2\text{NO}\}$ (**9**), $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{Cl}\}$ (**10**), $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{I}\}$ (**11**) and $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]W}(\text{CO})_3\text{CH}_3\}$ (**12**), were prepared through mono-demethylation of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ with 1 M equivalent of **5–8**, respectively [7].



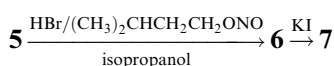
The IR data for complexes **1–12** in the CO and NO regions are listed in Table 1. In the case of complexes **6** and **7**, NO stretching bands were observed at higher frequencies than their unsubstituted parent complexes **2** and **3**.



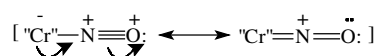
2. Results and discussion

2.1. Synthesis and characterization

Chlorination/nitrosylation of $(\eta^5\text{-carboxycyclopentadienyl})\text{dicarbonylnitrosylchromium}$ (cynichrodenoic acid) **5** in isopropanol, a novel method of replacing dicarbonyl with $(\text{NO})\text{Cl}$ ligand [2], produced **6** in 94% yield. Treatment of **6** with potassium iodide led to iodo product **7** in 91% yield.



3 by $\sim 20\text{--}40\text{ cm}^{-1}$. The shift correlated well with the trend of increasing tendency of electron-withdrawing ligand reduces the π back-bonding from Cr $d\pi$ -orbitals to the π^* orbitals of NO groups. However,



upon complexing to $\text{Cp}_2\text{Ti}(\text{CH}_3)-$, the $\nu(\text{NO})$ bands shifts back to lower energies by about $10\text{--}30\text{ cm}^{-1}$. The observation of lower frequencies of the NO bands indicates the π back-bonding to the NO ligands upon formation of

Table 1
IR spectra of 1–12

Compound	$\nu(\text{CO})$	$\nu(\text{NO})$	$\nu(\text{CO}_2)$
1	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{CO})_2\text{NO}$	2020 1945	1680
2	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{Cl}$		1805 1700
3	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{I}$		1810 1695
4	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{W}(\text{CO})_3\text{CH}_3$	2018 1927	
5	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{CO})_2\text{NO}$	2043 1947	1698
6	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{Cl}$		1832 1726 1682
7	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{I}$		1828 1734 1682
8	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{W}(\text{CO})_3\text{CH}_3$	2020 1915	1680
9	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{CO})_2\text{NO}\}$	2023 1927	1693 1642 1322
10	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{Cl}\}$		1822 1700 1640 1327
11	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{I}\}$		1817 1703 1646 1320
12	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]W}(\text{CO})_3\text{CH}_3\}$	2011 1918	1646 1313

bimetallic complexes was enhanced, as a result of stronger electron-donating of $\text{Cp}_2(\text{CH}_3)\text{Ti}$ -compared to hydrogen. In the $\text{Cp}_2\text{Ti}(\text{Cl})[\mu\text{-(C}_6\text{H}_4\text{R)}\text{Cr}(\text{CO})_3]$ system reported by

Lotz and coworkers [8] 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 $15\text{--}21\text{ cm}^{-1}$.

Table 2
 ^1H NMR data

Compound	Cp(Cr, W)		Ti-CH ₃	Cp(Ti)	W-CH ₃	Reference
	H(2,5)	H(3,4)				
1	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{CO})_2\text{NO}^{\text{a}}$	5.07 (s, 5)				[4a]
2	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{Cl}^{\text{a}}$	5.73 (s, 5)				[4c]
3	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{I}^{\text{a}}$	5.78 (s, 5)				[4c]
4	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{W}(\text{CO})_3\text{CH}_3^{\text{a}}$	5.30 (s, 5)			0.37	[3c]
5	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{CO})_2\text{NO}^{\text{a}}$	5.81 (t, 2)	5.30 (t, 2)			[20]
	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{NO}^{\text{b}}$	5.87 (t, 2)	5.36 (t, 2)			[4a]
6	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{Cl}^{\text{b}}$	6.36 (t, 2)	5.99 (t, 2)			This work
7	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{I}^{\text{b}}$	6.49 (t, 2)	6.08 (t, 2)			This work
8	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{W}(\text{CO})_3\text{CH}_3^{\text{a}}$	5.94 (t, 2)	5.78 (t, 2)		0.46	This work
	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{W}(\text{CO})_3\text{CH}_3^{\text{b}}$	5.94 (t, 2)	5.73 (t, 2)		0.48	[6]
9	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{CO})_2\text{NO}\}^{\text{a}}$	5.39 (t, 2)	5.00 (t, 2)	0.96	6.22	This work
10	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{Cl}\}^{\text{b}}$	5.87 (t, 2)	5.65 (t, 2)	1.01	6.25	This work
11	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{I}\}^{\text{a}}$	5.97 (t, 2)	5.70 (t, 2)	1.01	6.25	This work
12	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]W}(\text{CO})_3\text{CH}_3\}^{\text{a}}$	5.45 (t, 2)	5.34 (t, 2)	0.96	6.23	This work
	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]_2\text{Ti}(\text{CH}_3)[\text{O-C(O)H}]^{\text{c}}$		0.7	6.19		[10]

^a In CDCl_3 .

^b In CD_3COCD_3 .

^c In CD_2Cl_2 , relative to TMS.

Table 3
 $^{13}\text{C}\{^1\text{H}\}$ NMR data^a

Compound	Cp(Cr, W)			M-C \equiv O	C=O	Ti-CH ₃	Cp(Ti)	W-CH ₃
	C(1)	C(2,5)	C(3,4)					
1	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{CO})_2\text{NO}$	90.31 (C(1–5))		237.10				
2	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{Cl}$	103.02 (C(1–5))						
3	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{Cr}(\text{NO})_2\text{I}$	101.32 (C(1–5))						
4	$[\eta^5\text{-(C}_5\text{H}_5\text{)}]\text{W}(\text{CO})_3\text{CH}_3$	91.18 (C(1–5))		229.29, 216.12				–34.98
5	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{CO})_2\text{NO}$	94.74	95.60	93.36	236.37	165.54		
6	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{Cl}$	108.01	108.42	104.61		162.46		
7	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{NO})_2\text{I}$		106.85	103.67		163.00		
8	$[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{W}(\text{CO})_3\text{CH}_3$	97.51	94.57	95.37	228.99, 216.52	165.34		–32.61
9	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{CO})_2\text{NO}\}$	98.01	94.22	90.83	235.88	168.03	45.45	114.74
10	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{Cl}\}$	107.49	106.70	103.36		164.69	47.27	115.04
11	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]Cr}(\text{NO})_2\text{I}\}$	106.37	104.80	101.71		165.03	47.38	115.06
12	$\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{[OC(O)C}_5\text{H}_4\text{]W}(\text{CO})_3\text{CH}_3\}$		92.80	92.88				

^a Chemical shifts are reported in ppm with respect to internal Me_4Si .

They attributed this observation in terms of the high basicity of the $(C_6H_4R)Cr(CO)_3$ 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. The 1H and ^{13}C NMR spectra for complexes **1–12** are listed in Tables 2 and 3 [1,4b,5]. The chemical shifts of protons and carbons on Cp(Cr or W) of **9–12** occur at higher fields than those of the corresponding nuclei of **5–8** (Tables 2 and 3). This reflects an increasing electron density on the cyclopentadienyl ring ligand after complexing. In contrast to the upfield shift of the Cp(Cr) or Cp(W) ring, the chemical shifts (δ 6.22, 6.25, 6.25, 6.23 ppm) of Cp(Ti) protons occur at lower fields than those of $[\eta^5-(C_5H_5)_2Ti(CH_3)[O-C(O)H]]$ (δ 6.19 ppm) [9]. This reflects that the $(CO)_2(NO)Cr(C_5H_4^-)$, $(NO)_2(X)Cr(C_5H_4^-)$ ($X = Cl, I$) and $(CO)_3(CH_3)W(C_5H_4^-)$ are electron-withdrawing groups, compared to hydrogen. In a whole, that the transfer of electron density from $Cp_2Ti(CH_3)-$ moiety to the Cp(Cr) (or Cp(W)) moiety, raising the extent of π -back bonding from Cr (or W) metal center to the NO (or CO) ligands, resulting in the lower vibrational frequencies of NO (or CO)) is consistently revealed.

The assignments of ^{13}C NMR spectra of **6–12** (Table 3) were based on standard ^{13}C NMR correlation [10], 2D HetCOR (Fig. 1), the DEPT technique and by comparison with other metallo-aromatic systems [11]. One surprising finding in the study of ^{13}C spectra of **5–7** and **9–11** (Table 3) is that the high field and low field chemical shifts are assigned to C(3,4) and C(2,5), respectively, for electron-withdrawing carbonyl substituent on Cp(Cr) ring which is opposite to the assignment of ferrocene derivatives [4,11]. In ferrocenes the 3,4-positions of the substituted cyclopentadienyl ring are more sensitive to electron-withdrawing substituents by resonance, while in cynichrodenes the 2,5-positions of the substituted cyclopentadienyl ring are more sensitive to electron-withdrawing substituents.

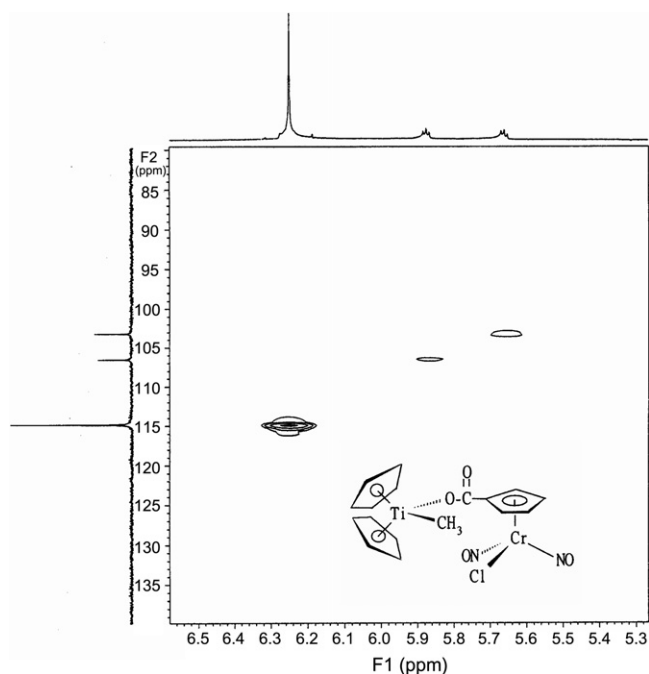
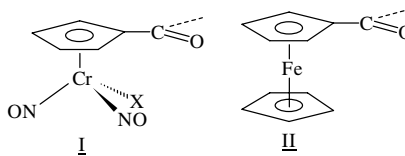
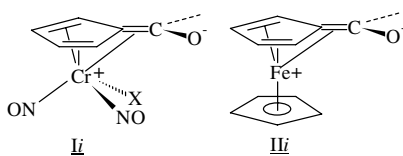
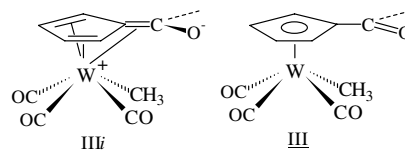


Fig. 1. 2D $^1H\{^{13}C\}$ HetCOR NMR spectrum of **10** in $CDCl_3$.

the opposite assignments were made for $CpW(CO)_3CH_3$ derivatives, **8** and **12**. Two factors, the 1st being the outer valence electrons of tungsten atom are much more shielded from the nucleus by the extra shell of electrons, d and f electrons, therefore much easier to be pushed about and more basic, than those for chromium atom, the second being the less electron-withdrawing property of CO than that of NO, may induce the greater extent of contribution of canonical form III_i than I_i to each of the corresponding structures III and I, and the opposite assignments between



The smaller contribution of canonical form I_i than II_i to each of the corresponding structures I and II may explain such behaviour. This is understandable in the destabilization of chromium cation because of the overall electron-withdrawing properties of two NO and X ligands. Therefore, in cyclopentadienyl chromium complexes (**5–7** and **9–11**), bearing an electron-withdrawing substituent, the inductive effect that deshields the nearby carbon (C(2,5)) atoms to a greater extent than the more distant 3- and 4- positions may explain the observed data collected in Table 3. However, for the same group VI metal,



chromium and tungsten Cp derivatives are made. On a whole, it may explain that for derivatives with electron-withdrawing substituents, an analogy was observed

between the shielding of C(2,5) and C(3,4) carbon atoms of CpW(CO)₃CH₃ derivatives and those of ferrocenes derivatives, while the opposite correlation was observed for the derivatives of cynchrodene **1**, CpCr(NO)₂Cl (**2**) and CpCr(NO)₂I (**3**).

An important advantage of the ¹³C NMR method over ¹H NMR spectroscopy is the relatively lower susceptibility of ¹³C chemical shifts to the effects of magnetically anisotropic groups and ring current [12]. Therefore ¹³C NMR spectra provide a clearer picture of the electron density distribution within a molecule than do proton NMR spectra. Thus, to obtain the unequivocal assignments of C(2,5) and C(3,4) on the Cp ring, the use of 2D HetCOR NMR spectroscopy is very instructive, especially for first-row metals and/or metals coordinated with ligands bearing strong electron-withdrawing property.

The unequivocal assignments of ¹³C chemical shifts for **10** were correlated well with the ab initio calculations from the X-ray data of **10**. The average charges of C(2,5) and C(3,4) are −0.1897 and −0.2486.

The molecular structure of **10** is shown in Fig. 2. Selected bond distances and angles are given in Table 4. The atomic coordinates of the non-hydrogen atoms are listed in Table 5. The Ti–O(3) distance of 1.977(2) Å is slightly longer than those in Cp₂Ti(CH₃){[OC(O)C₆H₅]Cr(CO)₃} (1.940(3) Å) [7] and Cp₂Ti{[OC(O)C₅H₄]Fe(CO)₂(CH₂C₆H₅)₂} (1.948 Å) [13]. The Ti–O(3)–C(6) angle of 137.1(2)° is smaller than those in Cp₂Ti(CH₃){[OC(O)C₆H₅]Cr(CO)₃} (149.6°) [7] and Cp₂Ti{[OC(O)C₅H₄]Fe(CO)₂(CH₂C₆H₅)₂} (143.7°) [13]. Comparatively, the longer Ti–O distance and the relatively smaller Ti–O–C angle indicates the less extent of Ti–O π-bonding in **10**, than those in Cp₂Ti(CH₃){[OC(O)C₆H₅]Cr(CO)₃} [7] and Cp C₅H₄]Fe(CO)₂Ti{[OC(O)–(CH₂C₆H₅)₂}. Which is conceivable due to the less extent of electron donating from the electron-deficient CpCr(NO)₂Cl moiety to the carboxylato oxygen, lessening π-donor tendency of the oxygen to Ti atom.

For CpCr(NO)₂Cl moiety of **10**, several important features are observed. The Cl atom is located at the site

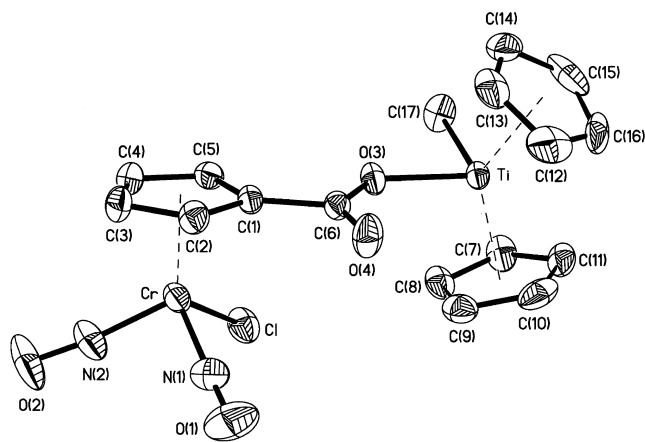


Fig. 2. Molecular configuration of **10**.

Table 4
Selected bond length (Å) and selected bond angles (°) for **10**

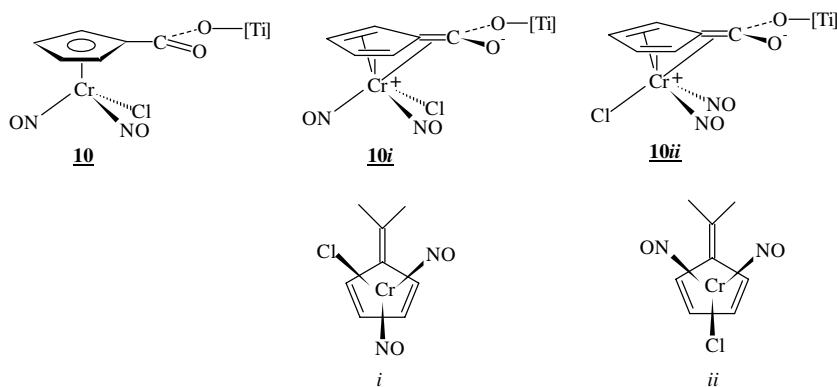
Cr–N(1)	1.710(4)	C(6)–O(4)	1.213(4)
Cr–N(2)	1.717(4)	Ti–O(3)	1.977(2)
Cr–Cl	2.3232(14)	Cr···C(6)	3.273
Ti–C(17)	2.178(4)	Cr–Cp	1.863
C(7)–C(11)	1.386(6)	O(1)···Cl	4.030
C(4)–C(5)	1.406(5)	O(2)···Cl	4.110
N(1)–O(1)	1.167(5)	Cp1···Ti	2.0562
N(2)–O(2)	1.165(5)	Cp2···Ti	2.0615
C(1)–C(6)	1.495(5)	Ti···O(4)	3.468
C(6)–O(3)	1.283(4)		
N(1)–Cr–N(2)	95.1(2)	O(4)–C(6)–O(3)	126.1(3)
N(1)–Cr–Cl	97.81(14)	O(4)–C(6)–C(1)	120.1(3)
N(2)–Cr–Cl	100.26(14)	O(3)–C(6)–C(1)	113.8(3)
O(1)–N(1)–Cr	170.0(4)	C(6)–O(3)–Ti	137.1(2)
O(2)–N(2)–Cr	170.2(4)	O(3)–Ti–C(17)	90.98(14)
C(5)–C(1)–C(6)	127.8(3)	Cp1–Ti–Cp2	132.78
C(2)–C(1)–C(6)	124.4(3)		

Table 5

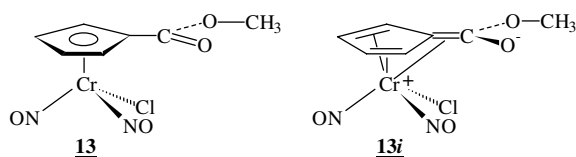
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Cr	2969(1)	5542(1)	1330(1)	46(1)
Ti	6993(1)	4046(1)	3581(1)	36(1)
Cl	3665(1)	3618(1)	1218(1)	63(1)
N(1)	1940(3)	5316(3)	2133(3)	66(1)
N(2)	1895(4)	5565(4)	487(3)	72(1)
O(1)	1270(4)	5332(4)	2712(3)	109(2)
O(2)	1178(4)	5756(4)	−76(3)	116(2)
O(3)	5975(2)	5107(2)	2836(2)	45(1)
O(4)	4511(3)	5939(3)	3603(2)	67(1)
C(1)	4544(3)	6277(3)	2084(2)	37(1)
C(2)	3592(4)	7132(3)	2025(3)	49(1)
C(3)	3409(4)	7406(4)	1132(3)	61(1)
C(4)	4234(4)	6750(4)	644(3)	61(1)
C(5)	4941(3)	6062(4)	1233(2)	47(1)
C(6)	5025(3)	5751(3)	2924(2)	42(1)
C(7)	6795(4)	1987(3)	3311(3)	61(1)
C(8)	5740(4)	2531(4)	2953(3)	57(1)
C(9)	5106(4)	3014(4)	3630(3)	60(1)
C(10)	5770(5)	2794(4)	4414(3)	72(1)
C(11)	6807(4)	2155(3)	4210(3)	61(1)
C(12)	7098(6)	5157(6)	4867(3)	85(2)
C(13)	7461(5)	5900(4)	4229(4)	72(2)
C(14)	8514(5)	5503(5)	3915(3)	73(2)
C(15)	8846(5)	4488(5)	4358(5)	92(2)
C(16)	7982(8)	4291(5)	4959(4)	101(3)
C(17)	8222(4)	3739(4)	2510(3)	63(1)

toward the exocyclic organic carbonyl carbon with twist angle of 59.8°. The twist angle of N(1) and N(2) is 59.9 and 178.1°, respectively. The preference for the unsymmetrical isomer *i* to the symmetrical isomer *ii* may be related to the ability of the exocyclic double bond to donate electron density to the chromium atom, (reestablishing the favored 18-electron count) such that it is transoid to the better π-accepting ligand, i.e. NO⁺. As a result, the exocyclic



carbons C is slightly bent towards the chromium atom with θ angle of 0.2° . The exocyclic C–C bond is $1.495(5) \text{ \AA}$ [C(1)–C(6)], considerably longer than that found in **13** [η^5 -(C₅H₄–COOCH₃)Cr(NO)₂Cl ($1.465(8) \text{ \AA}$) [1], but is shorter than that found in [η^5 -(C₅H₄–CH=CH₂)]Fe(η^5 -C₅H₄)-CH₂(η^5 -C₅H₄)Cr(NO)₂Cl ($1.507(6) \text{ \AA}$) [14]. The smaller



contribution of canonical form **10i** than **13i** to each of the corresponding structures **10** and **13** may explain such behaviour. The electron donating Cp₂Ti(CH₃)– increases the extent of resonance between the two carboxylate oxygens, thus reduces the contribution of canonical form **10i** to **10** leads to longer exocyclic C(1)–C(6) bond length.

The comparably long and weak Ti–O(3) bond, short distance of Cr–cen.(Cp(Cr)) (1.863 \AA in **10** vs. 1.870 \AA in **13**) [1], short bond length of Cr–N ($1.676(6)$, $1.718(5) \text{ \AA}$ in **10** vs. $1.705(5)$, $1.712(5) \text{ \AA}$ in **13**) and long N≡O bond length ($1.163(7)$, $1.177(8) \text{ \AA}$ in **10** vs. $1.160(7)$, $1.163(6) \text{ \AA}$ in **13**), consistently demonstrate that there is an electron flow from OC(O) to the Cp(Cr) ring and then passes it to the Cr atom which in turn π -back bonds to π^* orbitals of nitrosyl groups to give longer N–O bond lengths.

The carbonyl plane [C(1), C(6), O(3), O(4)] is turned away from the Cp(Cr) ring by 7.5° as compared with 1.2 and 0.3° found in (η^5 -C₅H₄–COOCH₃)Cr(NO)₂Cl and (η^5 -C₅H₄–COOCH₃)Cr(NO)₂I [1].

3. Experimental

All the syntheses were carried out under nitrogen by the use of Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and deoxygenated nitrogen was dried over molecular sieves (3 \AA) and P₂O₅. Hexane, pentane, benzene, and dichloromethane were dried over calcium hydride and freshly distilled under nitrogen.

Table 6

Crystal data and structure refinement for ic3272

Identification code	ic3272
Empirical formula	C17 H17 Cl Cr N2 O4 Ti
Formula weight	448.68
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	10.956(3)
<i>b</i> (Å)	11.359(2)
<i>c</i> (Å)	15.262(5)
α (°)	90
β (°)	91.76(3)
γ (°)	90
Volume (Å ³)	1898.4(9)
<i>Z</i>	4
<i>D</i> _{Calc} (Mg/m ³)	1.570
Absorption coefficient (mm ⁻¹)	1.157
<i>F</i> (000)	912
Crystal size (mm)	0.50 × 0.45 × 0.25
Theta range for data collection (°)	2.24–25.00
Index ranges	$-13 \leq h \leq 12$, $0 \leq k \leq 13$, $0 \leq l \leq 18$
Reflections collected	3334
Independent reflections	3334
Completeness to theta = 25.00°	99.9%
Absorption correction	Psi-scan
Maximum and minimum transmission	0.7607 and 0.5953
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3334/0/236
Goodness-of-fit on <i>F</i> ²	1.015
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.1243
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0746, <i>wR</i> ₂ = 0.1389
Largest difference in peak and hole (e Å ⁻³)	0.570 and -0.458

Diethyl ether was dried over sodium and redistilled under nitrogen from sodium-benzophenone ketyl. All the other solvents were used as commercially obtained.

Column chromatography was carried out under nitrogen with Merck Kiesel-gel 60. The silica gel was heated with a heat gun during mixing in a rotary evaporator attached to a vacuum pump for 1 h to remove water and oxygen. The silica gel was then stored under nitrogen until use.

¹H and ¹³C NMR were acquired on a Varian Unity-300 spectrometer. Chemical shifts were referenced to tetra-

methylsilane. IR spectra were recorded a Perkin–Elmer Fourier transform IR 1725X spectrophotometer. Microanalyses were carried out by the Microanalytic Laboratory of the National Chung Hsing University.

Complexes **5** [15], **8** [6], and **14** [6] were prepared by following the published procedures. The characterizations of **5**, **8**, and **14** are given here.

$[\eta^5\text{-}(\text{C}_5\text{H}_4\text{COOH})\text{Cr}(\text{CO})_2\text{NO}]$ (**5**). ^1H NMR (CD_3COCD_3): δ 5.36 (2H, t, Cp H(3,4)); δ 5.87 (2H, t, Cp H(2,5)). ^{13}C NMR (CD_3COCD_3): δ 93.36 (Cp, C(3,4)); δ 94.74 (Cp, C(1)); 95.60 (Cp, C(2,5)); δ 165.54 ($-\text{C}(\text{O})-$); δ 236.37 (Cr–CO).

$[\eta^5\text{-}(\text{C}_5\text{H}_4\text{COOH})\text{W}(\text{CO})_3\text{CH}_3]$ (**8**). ^1H NMR (CDCl_3): δ 0.46 (3H, s, W–CH₃); δ 5.78 (2H, t, Cp H(3,4)); δ 5.94 (2H, t, Cp H(2,5)). ^{13}C NMR (CDCl_3): δ –32.61 (W–CH₃); δ 94.57 (Cp, C(2,5)); δ 95.37 (Cp, C(3,4)); δ 97.51 (Cp, C(1)); δ 165.34 ($-\text{C}(\text{O})-$); δ 216.52, 228.99 (W–CO).

$[\eta^5\text{-}(\text{C}_5\text{H}_4\text{-COOCH}_3)\text{W}(\text{CO})_3\text{CH}_3]$ (**14**). ^1H NMR (CDCl_3): δ 0.48 (3H, s, W–CH₃); δ 3.83 (3H, –COOCH₃); δ 5.46 (2H, t, Cp H(3,4)); δ 5.80 (2H, t, Cp H(2,5)). ^{13}C NMR (CDCl_3): δ –32.52 (W–CH₃); δ 52.20 (O–CH₃); δ 92.89 (Cp, C(2,5)); δ 93.17 (Cp, C(3,4)); δ 95.64 (Cp, C(1)); δ 164.54 ($-\text{C}(\text{O})-$); δ 214.09, 226.62 (W–CO).

3.1. Preparation of $(\eta^5\text{-carboxycyclopentadienyl})\text{-chlorodinitrosylchromium}$ (**6**)

Through a solution of $(\eta^5\text{-Carboxycyclopentadienyl})\text{dicarbonylnitrosylchromium}$ **5** (8.0 g, 32.37 mmol) in 200 ml of isopropanol, was bubbled hydrogen chloride for 10 min. After cooling to 0–10 °C, isoamyl nitrite (5.84 ml, 43.52 mmol) was added slowly (dark green solution resulted) and the reaction mixture was stirred for 40 min. After removing the solvent under vacuum, the residue was washed several times with distilled water. Compound $(\eta^5\text{-carboxycyclopentadienyl})\text{chlorodinitrosylchromium}$ (**6**) (7.78 g, 94%) was obtained after vacuum drying. An analytical sample (granular black gleaming crystal) m.p. 181 °C, was obtained by recrystallization using the solvent expansion method from hexane:tetrahydrofuran (5:2) at 0 °C for 48 h.

Anal. Calc. for $\text{C}_6\text{H}_5\text{O}_4\text{N}_2\text{ClCr}$: C, 28.09; H, 1.96; N, 10.92. Found: C, 28.28; H, 2.20; N, 10.48%. Proton NMR (CD_3COCD_3): δ (relative intensity, multiplicity, assignment): 5.99 (2H, t, Cp H(3,4)); 6.36 (2H, t, Cp H(2,5)). Carbon-13 NMR (CD_3COCD_3): δ (assignment): 104.61 (Cp, C(3,4)); 108.01 (Cp, C(1)); 108.42 (Cp, C(2,5)), 164.46 ($-\text{C}(\text{O})-$). IR (KBr): ν (cm^{-1}) (intensity): 3200–2400 (m, broad), 1832(vs), 1726(vs), 1682(vs), 1490(s), 1310(s), 1180(s). Mass spectrum: m/z 256 (M^+).

3.2. Preparation of $(\eta^5\text{-carboxycyclopentadienyl})\text{iododinitrosylchromium}$ (**7**)

To a stirred solution of $(\eta^5\text{-carboxycyclopentadienyl})\text{chlorodinitrosylchromium}$ (**6**) (1.0 g, 3.90 mmol) in 50 ml of methanol, potassium iodide (1.0 g, 6.02 mmol)

was added. The reaction mixture was stirred for 40 min at room temperature. The solvent was then removed under vacuum. The residue was washed with distilled water several times. Compound $(\eta^5\text{-carboxycyclopentadienyl})\text{iododinitrosylchromium}$ (**7**) (1.23 g, 91%) was obtained after vacuum drying. An analytical sample (granular black gleaming crystal), m.p. 197–201 °C, was obtained by recrystallization using the solvent expansion method from hexane:tetrahydrofuran (5:2) at 0 °C for 48 h.

Anal. Calc. for $\text{C}_6\text{H}_5\text{O}_4\text{N}_2\text{ICr}$: C, 20.71; H, 1.45; N, 8.05. Found: C, 20.93; H, 1.51; N, 7.82%. Proton NMR (CD_3COCD_3): δ (relative intensity, multiplicity, assignment): 6.08 (2H, t, Cp H(3,4)); 6.49 (2H, t, Cp H(2,5)). Carbon-13 NMR (CD_3COCD_3): δ (assignment): 103.67 (Cp, C(3,4)); 106.85 (Cp, C(2,5)); 163.00 ($-\text{C}(\text{O})-$). IR (KBr): ν (cm^{-1}) (intensity): 3200–2500 (m, broad), 1828(vs), 1734(vs), 1682(vs). Mass spectrum: m/z 348 (M^+).

3.3. Preparation of $\text{bis}(\eta^5\text{-cyclopentadienyl})\text{-}(\text{cynichrodenoato})\text{methyltitanium}$ (**9**)

As this product is light sensitive, all operations were carried out with the exclusion of light. To a solution of dicarbonyl $(\eta^5\text{-carboxycyclopentadienyl})\text{nitrosylchromium}$ (**5**) (0.38 g, 1.54 mmol) in 80 ml of dichloromethane, bis- $(\eta^5\text{-cyclopentadienyl})\text{dimethyltitanium}$ (0.32 g, 1.54 mmol) was added in an ice bath. The resulting solution was stirred at 0 °C for 2 h and then warmed slowly to room temperature. The reaction solution was concentrated to a residue and then washed with *n*-pentane twice. Compound bis- $(\eta^5\text{-cyclopentadienyl})\text{(cynichrodenoato)methyltitanium}$ (**9**) (0.54 g, 80%); m.p., 84–86 °C) was obtained after vacuum drying. An analytical sample (an orange gleamy needle) was prepared by recrystallization using the solvent expansion method from benzene:*n*-hexane (1:2) at 0 °C for 48 h.

Anal. Calc. for $\text{C}_{19}\text{H}_{17}\text{O}_5\text{NTiCr}$: C, 51.95; H, 3.90; N, 3.19. Found: C, 52.15; H, 3.74; N, 3.26%. Proton NMR (CDCl_3): δ (relative intensity, multiplicity, assignment): 0.96 (3H, s, –CH₃); 5.00 (2H, t, Cp(Cr) H(3,4)); 5.39 (2H, t, Cp(Cr) H(2,5)), 6.22 (10H, s, Cp(Ti)). Carbon-13 NMR (CDCl_3): δ (assignment): 45.45 ($-\text{CH}_3$); 90.83 (Cp(Cr), C(3,4)); 94.22 (Cp(Cr), C(2,5)); 98.01 (Cp(Cr), C(1)); 114.74 (Cp(Ti)); 168.03 ($-\text{C}(\text{O})-$); 235.88 (Cr–C≡O). IR (KBr): ν (cm^{-1}) (intensity): 2023(s), 1927(s), 1693(s), 1642(s), 1322(s). Mass spectrum: m/z 424 ($\text{M}-\text{CH}_3$)⁺.

3.4. Preparation of $[\text{chlorodinitrosylchromium}(\eta^5\text{-cyclopentadienylcarboxylato})]\text{bis}(\eta^5\text{-cyclopentadienyl})\text{-methyltitanium}$ (**10**)

As this product is light sensitive, all operations were carried out with the exclusion of light. To a solution of $(\eta^5\text{-carboxycyclopentadienyl})\text{chlorodinitrosylchromium}$ (**6**) (0.59 g, 2.30 mmol) in 80 ml of dichloromethane, bis- $(\eta^5\text{-cyclopentadienyl})\text{dimethyltitanium}$ (0.48 g, 2.31 mmol) was added in an ice bath. The resulting solution was stirred

at 0 °C for 2 h and then warmed slowly to room temperature. The reaction solution was concentrated to a residue and then washed with *n*-pentane twice. Compound [chlorodinitrosylchromium(η^5 -cyclopentadienylcarboxylato)] bis(η^5 -cyclopentadienyl)methyltitanium (**10**) (0.65 g, (63%); d.p., 192 °C) was obtained after vacuum drying as a black solid. An X-ray sample (a black gleamy needle) was prepared by recrystallization using the solvent expansion method from dichloromethane:*n*-hexane (1:2) at 0 °C for 48 h.

Anal. Calc. for C₁₇H₁₇O₄N₂ClTiCr: C, 45.50; H, 3.82; N, 6.24. Found: C, 44.92; H, 4.09; N, 6.83%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 1.01 (3H, s, -CH₃); 5.65 (2H, t, Cp(Cr) H(3,4)); 5.87 (2H, t, Cp(Cr) H(2,5)), 6.25 (10H, s, Cp(Ti)). Carbon-13 NMR (CDCl₃): δ (assignment): 47.27 (-CH₃); 103.36 (Cp(Cr), C(3,4)); 106.70 (Cp(Cr), C(2,5)); 107.49 (Cp(Cr), C(1)); 115.04 (Cp(Ti)); 164.69 (-C(O)-). IR (KBr): ν (cm⁻¹) (intensity): 1822(s), 1700(s), 1640(s), 1382(w), 1327(s). Mass spectrum: *m/z* 433 (M-CH₃)⁺.

3.5. Preparation of bis(η^5 -cyclopentadienyl)-[iododinitrosylchromium(η^5 -cyclopentadienylcarboxylato)]methyltitanium (**11**)

As this product is light sensitive, all operations were carried out with the exclusion of light. To a solution of (η^5 -carboxycyclopentadienyl)-iododinitrosylchromium (**7**) (0.79 g, 2.27 mmol) in 80 ml of dichloromethane, bis(η^5 -cyclopentadienyl)dimethyltitanium (0.47 g, 2.27 mmol) was added in an ice bath. The resulting solution was stirred at 0 °C for 2 h and then warmed slowly to room temperature. The reaction solution was concentrated to a residue and then washed with *n*-pentane twice. Compound bis(η^5 -cyclopentadienyl)[iododinitrosylchromium-(η^5 -cyclopentadienylcarboxylato)]methyltitanium (**11**) (0.98 g, (80%); d.p., 124 °C) was obtained after vacuum drying as a black solid. An analytical sample (a black gleamy needle) was prepared by recrystallization using the solvent expansion method from dichloromethane:*n*-hexane (1:2) at 0 °C for 48 h.

Anal. Calc. for C₁₇H₁₇O₄N₂ITiCr: C, 37.80; H, 3.17; N, 5.19. Found: C, 38.18; H, 3.21; N, 5.41%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 1.01 (3H, s, -CH₃); 5.70 (2H, t, Cp(Cr) H(3,4)); 5.97 (2H, t, Cp(Cr) H(2,5)), 6.25 (10H, s, Cp(Ti)). Carbon-13 NMR (CDCl₃): δ (assignment): 47.38 (-CH₃); 101.71 (Cp(Cr), C(3,4)); 104.80 (Cp(Cr), C(2,5)); 106.37 (Cp(Cr), C(1)); 115.06 (Cp(Ti)); 165.03 (-C(O)-). IR (KBr): ν (cm⁻¹) (intensity): 1817(s), 1703(s), 1646(s), 1378(w), 1320(s). Mass spectrum:*m/z* 525(M-CH₃)⁺.

3.6. Preparation of [tricarbonylmethyltungsten(η^5 -cyclopentadienylcarboxylato)]-bis(η^5 -cyclopentadienyl)-methyltitanium (**12**)

As this product is light sensitive, all operations were carried out with the exclusion of light. To a solution of tricarbonyl(η^5 -carboxycyclopentadienyl)methyltungsten (**8**) (0.53 g, 1.35 mmol) in 80 ml of dichloromethane, bis(η^5 -cyclopentadienyl)dimethyltitanium (0.28 g, 1.35 mmol) was added in an ice bath. The resulting solution was stirred at 0 °C for 2 h and then warmed slowly to room temperature. The reaction solution was concentrated to a residue and then washed with *n*-pentane twice. Compound [tricarbonylmethyltungsten(η^5 -cyclopentadienylcarboxylato)] bis(η^5 -cyclopentadienyl)methyltitanium (**12**) (0.35 g, (44%); d.p., 120 °C) was obtained after vacuum drying. An analytical sample (a yellow gleamy crystal) was prepared by recrystallization using the solvent expansion method from benzene:*n*-hexane (1:2) at 0 °C for 48 h.

Anal. Calc. for C₂₁H₂₀O₅TiCr: C, 43.18; H, 3.45. Found: C, 42.82; H, 3.50%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 0.48 (3H, s, W-CH₃); 0.96 (3H, s, -CH₃); 5.34 (2H, t, Cp(W) H(3,4)); 5.45(2H, t, Cp(W) H(2,5)), 6.23 (10H, s, Cp(Ti)). Carbon-13 NMR (CDCl₃): δ (assignment): 92.80 (Cp(W), C(2,5)); 92.88 (Cp(Cr), C(3,4)). IR (KBr): ν (cm⁻¹) (intensity): 2011 (s), 1918(s), 1646(s), 1378 (w), 1313 (s). Mass spectrum: *m/z* 569 (M-CH₃)⁺.

Anal. Calc. for C₂₁H₂₀O₅TiCr: C, 43.18; H, 3.45. Found: C, 42.82; H, 3.50%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 0.48 (3H, s, W-CH₃); 0.96 (3H, s, -CH₃); 5.34 (2H, t, Cp(W) H(3,4)); 5.45(2H, t, Cp(W) H(2,5)), 6.23 (10H, s, Cp(Ti)). Carbon-13 NMR (CDCl₃): δ (assignment): 92.80 (Cp(W), C(2,5)); 92.88 (Cp(Cr), C(3,4)). IR (KBr): ν (cm⁻¹) (intensity): 2011 (s), 1918(s), 1646(s), 1378 (w), 1313 (s). Mass spectrum: *m/z* 569 (M-CH₃)⁺.

3.7. X-ray diffraction analyses of **10**

The intensity data were collected on a CAD-4 diffractometer with a graphite monochromator (Mo K α radiation). $\theta - 2\theta$ scan data were collected at room temperature (24 °C). The data were corrected for absorption, Lorentz and polarization effects. The absorption correction is according to the empirical psi rotation. The details of crystal data and intensity collection are summarized in Table 6.

The structures were solved by direct methods and were refined by full matrix least squares refinement based on *F* values. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were positioned at calculated coordinate with a fixed isotropic thermal parameter ($U = U(\text{attached atom}) + 0.01 \text{ \AA}^2$). Atomic scattering factors and corrections for anomalous dispersion were from International Tables for X-ray crystallography [16]. All calculations were performed on a PC computer using SHELX software package [17].

3.8. Computational method

In this study, we use the B3LYP hybrid method involving the three-parameter Becke exchange functional [18] and a Lee–Yang–Parr correlation functional [19]. All calculations are performed with the GAUSSIAN 03 program using the 6-311G(d,p) basis set [20]. The geometries for **10** is taken from the crystallographic data. The atomic charges have been analyzed using the natural population analysis (NPA) which yields reliable atomic charges and natural bond orbital (NBO) calculations [21]. An important feature of the NBO method is that the presence of diffuse functions in the basis sets does not affect the results.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.10.059](https://doi.org/10.1016/j.jorganchem.2007.10.059).

References

- [1] Y.-P. Wang, Y.-H. Yang, S.-L. Wang, F.-L. Liao, *J. Organomet. Chem.* 419 (1991) 325.
- [2] Y.-P. Wang, J.-M. Hwu, *J. Organomet. Chem.* 399 (1990) 141.
- [3] (a) J. Koernich, S. Haubold, J. He, O. Reimelt, J. Heck, *J. Organomet. Chem.* 584 (1999) 329;
(b) S. Top, E.B. Kaloun, S. Toppi, A. Herrbach, M.J. McGlinchey, G. Jaouen, *Organometallics* 20 (2001) 4554;
(c) O.G. Adeyemi, N.J. Coville, *Organometallics* 22 (2003) 2284.
- [4] (a) Y.-P. Wang, T.-S. Lin, Y.-H. Yang, J.-H. Liaw, S.-L. Wang, F.-L. Liao, Y.-J. LuWang, *J. Organomet. Chem.* 503 (1995) 35;
(b) Y.-P. Wang, X.-H. Lui, B.-S. Lin, W.-D. Tang, T.-S. Lin, J.-H. Liaw, Y. Wang, Y.-H. Liu, *J. Organomet. Chem.* 575 (1999) 310;
(c) Y.-P. Wang, H.-L. Leu, Y. Wang, H.-Y. Cheng, T.-S. Lin, *J. Organomet. Chem.* 692 (2007) 3340.
- [5] E.W. Slocum, C.R. Ernst, *Adv. Organomet. Chem.* 10 (1972) 79.
- [6] D.W. Macomber, M.D. Rausch, *J. Organomet. Chem.* 258 (1983) 331.
- [7] H.-M. Gau, C.-T. Chen, T.-T. Jong, M.-Y. Chein, *J. Organomet. Chem.* 448 (1993) 99.
- [8] (a) P.H. van Rooyen, M. Schindebutte, S. Lotz, *Organometallics* 11 (1992) 1104;
(b) M.-K. Jiang, C.-C. Lin, H.-M. Gau, *J. Organomet. Chem.* 539 (1997) 155.
- [9] D.H. Gibson, Y. Ding, R.L. Miller, B.A. Sleadd, M.S. Mashuta, J.F. Richardson, *Polyhedron* 18 (1999) 1189.
- [10] J.B. Stotter (Ed.), *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972.
- [11] B.E. Mann, *Adv. Organomet. Chem.* 12 (1974) 135.
- [12] A.A. Koridze, P.V. Petrovskii, A.I. Mokhov, A.I. Lutsenko, *J. Organomet. Chem.* 136 (1977) 57.
- [13] H.-M. Gau, C.-C. Schei, L.-K. Liu, L.-H. Luh, *J. Organomet. Chem.* 435 (1992) 43.
- [14] Y.-P. Wang, T.-S. Lin, R.-S. Shyu, J.-M. Hwu, Y. Wang, M.-C. Cheng, *J. Organomet. Chem.* 271 (1989) 57.
- [15] D.W. Macomber, M.D. Rausch, *Organometallics* 2 (1983) 1523.
- [16] *International Tables for X-ray Crystallography*, vol. IV, Kynoch, Birmingham, UK, 1974.
- [17] E.J. Gabe, Y. LePage, J.-P. Charland, F.L. Lee, P.S. White, *J. Appl. Crystallogr.* 22 (1989) 384.
- [18] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [19] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [20] GAUSSIAN 03, Revision C.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian Inc., Wallingford CT, 2004.
- [21] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (6) (1988) 899.