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$Cp_2Ti\{[OC(O)C_5H_4]Cr(CO)_2NO]\}_2$ and $Cp_2Ti\{[(OC(O)C_5H_4]Cr(NO)_2X\}_2$ syntheses and spectra of chromium–titanium complexes bridged by carboxylate substituted cyclopentadienyl group

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ABSTRACT

Complete demethylation of $Cp_2Ti(CH_3)_2$ in dichloromethane with 2 M equivalent of $[\eta^5\text{-}(C_5H_4COOH)]Cr(CO)_2NO$ (**5**), $[\eta^5\text{-}(C_5H_4COOH)]Cr(NO)_2X]$ (X = Cl **6**, X = I **7**), and $[\eta^5\text{-}(C_5H_4COOH)]W(CO)_3CH_3$ (**8**); gives $Cp_2Ti\{[OC(O)C_5H_4]Cr(CO)_2NO\}_2$ (**13**), $Cp_2Ti\{[OC(O)C_5H_4]Cr(NO)_2Cl\}_2$ (**14**), $Cp_2Ti\{[OC(O)C_5H_4]Cr(NO)_2I\}_2$ (**15**),and $Cp_2Ti\{[OC(O)C_5H_4]W(CO)_3CH_3\}_2$ (**16**), respectively. The chemical shifts of C(2)–C(5) carbon atoms of compounds **13**–**15** have been assigned using two-dimensional HetCOR NMR spectroscopy. The assigned chemical shifts were compared with the NMR data of their analogues of ferrocene, and the opposite correlation on the assignments was observed for cynichrodenoyl moieties.

1. Introduction

Albeit the chemistry of titanocene dicarboxylate has been thoroughly explored [1], the number of isolated and well characterized mixed-metal complexes are only four, $Cp_2Ti\{[OC(O)C_5H_4]Fe(CO)_2(CH_2C_6H_5)\}_2$ [2], $Cp_2Ti\{[OC(O)C_6H_5]Cr(CO)_3\}_2$ [3], $Cp_2Ti\{[OC(O)C_5H_4]Fe(CO)_2(C_5H_4)Mn(CO)_3\}_2$ [4], and $Cp_2Ti\{[OC(O)C_5H_4]Fe(C_5H_4PPh_2)\}_2$ [5],

The potential ability of the early transition metal to activate a small molecule such as CO on the late transition metal centers [6] and the established antitumor or antiinflammatory activities of titanocene carboxylates or titanocene dicarboxylates [7] have prompted us to synthesize complexes **9**–**16**. Complexes **9**–**12** were reported earlier [8]. The facts that titanocene dicarboxylates are more stable than monocarboxylates [9] and dicarboxylates are more active than monocarboxylates as precursors for ethylene polymerization [10] made the synthesis of complexes **13**–**16** more promising.

Earlier [8], we reported the opposite correlation on the assignments of C(2,5) and C(3,4) on the Cp ring between (cyclopentadienyl) dicarbonylnitrosylchromium (hereafter called cynichrodene) and ferrocene derivatives bearing electron-withdrawing substituents in ^{13}C NMR spectra. The spectra data obtained from complexes **13**–**15** will further confirm the hypothesis we proposed to elucidate those opposite correlation.

Herein, we report thorough spectral studies on **13**–**16**. Each complex appears to be the first example of titanocene dicarboxylate containing Cp functionally substituted derivative of $CpCr(CO)_2NO$, $CpCr(NO)_2Cl$, $CpCr(NO)_2I$, and $CpW(CO)_3CH_3$ moiety, respectively. ^1H and ^{13}C NMR spectral comparison between complexes **1**–**16** are also included.

2. Results and discussion

2.1. Synthesis and characterization

Complexes, $Cp_2Ti(CH_3)\{[OC(O)C_5H_4]Cr(CO)_2NO\}$ **9**, $Cp_2Ti(CH_3)\text{-}\{[OC(O)C_5H_4]Cr(NO)_2Cl\}$ **10**, $Cp_2Ti(CH_3)\{[OC(O)C_5H_4]Cr(NO)_2I\}$ **11** and $Cp_2Ti(CH_3)\{[OC(O)C_5H_4]W(CO)_3CH_3\}$ **12**, were prepared through mono-demethylation of $Cp_2Ti(CH_3)_2$ with 1 M equivalent of **5**–**8**, respectively [8]. With 2 M equivalent, complete demethylation of

$$Cp_2Ti(CH_3)_2 + \mathbf{5}(\mathbf{6},\mathbf{7},\mathbf{8}) \rightarrow \mathbf{9}(\mathbf{10},\mathbf{11},\mathbf{12}) + CH_4$$

$Cp_2Ti(CH_3)_2$ gave complexes, $Cp_2Ti\{[OC(O)C_5H_4]Cr(CO)_2(NO)\}_2$ **13**, $Cp_2Ti\{[OC(O)C_5H_4]Cr(NO)_2Cl\}_2$ **14**, $Cp_2Ti\{[OC(O)C_5H_4]Cr(NO)_2I\}_2$ **15** and $Cp_2Ti\{[OC(O)C_5H_4]W(CO)_3CH_3\}_2$ **16**.

$$Cp_2Ti(CH_3)_2 + 2\ \mathbf{5}(\mathbf{6},\mathbf{7},\mathbf{8}) \rightarrow \mathbf{13}(\mathbf{14},\mathbf{15},\mathbf{16}) + 2CH_4$$

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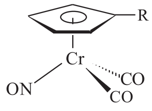

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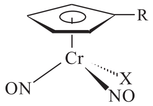

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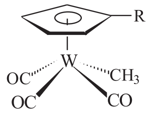

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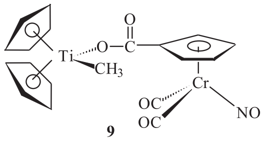

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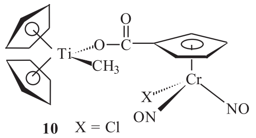

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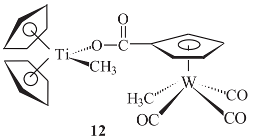

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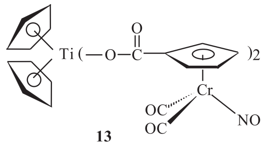

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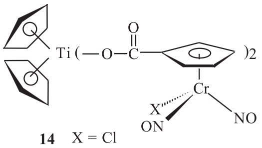

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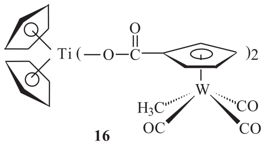

16

IR stretching bands of carbonyl, nitrosyl and carboxylate groups of the complexes are listed in Table 1. Each of **9** and **13** exhibits two terminal carbonyl stretching bands, the symmetric mode occurring at 2023 and 2017 cm^{-1} and the asymmetric mode at 1927 and 1947 cm^{-1}, respectively. The nitrosyl stretching band is observed at 1693 and 1704 cm^{-1}, respectively. For each of complexes **10, 11, 14,** and **15**, two terminal nitrosyl stretching bands were found, the symmetric mode occurring at 1811–1822 cm^{-1} and the asymmetric mode at 1700–1712 cm^{-1}. And for complexes **12** and **16**, two terminal carbonyl stretching bands were found for each. It is worth noting that upon complexing $Cp_2Ti(CH_3)$–(or Cp_2Ti–), the ν(NO) bands shift to lower frequencies by about 10–30 cm^{-1}. The observation indicates the π back-bonding to the NO ligands upon formation of bimetallic complexes was enhanced, as a result of stronger electron-donation of $Cp_2(CH_3)Ti$–(or Cp_2Ti–) compared to hydrogen. For all the complexes **9**–**16**, the ν(CO_2(asym)) at 1630–1646 cm^{-1} and ν (CO_2(sym)) at 1300–1327 cm^{-1} with Δν of ∼320 cm^{-1} suggest monodentate binding mode for all the carboxylate groups [12].

The ^1H and ^{13}C NMR spectra for complexes **1**–**16** are listed in Tables 2 and 3 [8]. Complexes $Cp_2Ti(CH_3)$ [OC(O)H], $Cp_2Ti[OC(O)H]_2$ [12], $Cp_2Ti\{[OC(O)C_5H_4]Fe(CO)_2(CH_2C_6H_5)\}_2$ [2], and $Cp_2Ti\{[OC(O)C_6H_5]Cr(CO)_3\}_2$ [3] are also listed for the purpose of comparison. The ^1H NMR spectrum of **13** exhibits an AA'XX' pattern for Cp(Cr), as is typical of similarly substituted cyclopentadienyl ring protons in many other metallo-aromatic systems [13,14]. The spectrum consists of a pair of apparent triplets, in which the downfield triplet, resonating at δ 5.65, can be assigned to the H(2,5) protons. This assignment is made on the basis of two reasons. The first is that the protons nearest the electron-withdrawing carbonyl group would be expected to be deshielded to a greater extent than the protons on the more distant 3- and 4- positons [15]. Analogous assignments have been made unequivocally for monosubstituted ferrocenes from the NMR spectra of 2,5-dideuterioferrocene derivatives [16]. The second is the strong diamagnetic anisotropic effect of the carbonyl on the ring protons. Closer to the carbonyl, the 2- and 5- protons were deshielded to a greater extent than those remote 3- and 4- protons [15]. The chemical shifts of protons and carbons on Cp(Cr or W) of **9**–**16** 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 and *δ* 0.96, 1.01, 1.01, 0.96 ppm) of Cp(Ti) and CH_3 protons in complexes **9**–**12** occur at lower field than those of $Cp_2Ti(CH_3)[OC(O)H]$ (*δ* 6.19 and 0.70 ppm) [12]. The same trend, chemical shifts (*δ* 6.57, 6.63, 6.62, 6.59 ppm) of Cp(Ti) in complexes **13**–**16** at lower field than that of $Cp_2Ti[OC(O)H]_2$ (*δ* 6.55 ppm) [12], was also observed. 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. The chemical shifts of protons and carbons on Cp(Cr) and Cp(Ti) for monocarboxylates **9**–**11**, which bear a methyl group on the Ti, appear relatively upfield compared with those for dicarboxylates **13**–**16**. This phenomenon reflects that $(CO)_2(NO)Cr(C_5H_4COO$–), $(NO)_2(X)Cr(C_5H_4COO$–) (X = Cl, I) and $(CO)_3(CH_3)W(C_5H_4COO$–) are less electron-donating groups, compared to methyl group, toward Ti metal. In a whole, that the transfer of electron density from $Cp_2Ti(CH_3)$–(or Cp_2Ti–) moiety to the Cp(Cr) (or Cp(W)) moiety, shifting the protons and carbons on Cp(Cr) (or Cp(W)) to higher fields and raising the extent of π-back

Table 1
IR spectra of **1**–**16**.

		ν(CO)		ν(NO)		ν(CO_2)	
1	[η^5-(C_5H_5)]$Cr(CO)_2NO$	2020	1945	1680			
2	[η^5-(C_5H_5)]$Cr(NO)_2Cl$			1805	1700l		
3	[η^5-(C_5H_5)]$Cr(NO)_2I$			1810	1695		
4	[η^5-(C_5H_5)]$W(CO)_3CH_3$	2018	1927				
5	[η^5-(C_5H_4COOH)]$Cr(CO)_2NO$	2043	1947	1698			
6	[η^5-(C_5H_4COOH)]$Cr(NO)_2Cl$			1832	1726	1682	
7	[η^5-(C_5H_4COOH)]$Cr(NO)_2I$			1828	1734	1682	
8	[η^5-(C_5H_4COOH)]$W(CO)_3CH_3$	2020	1915			1680	
9	$Cp_2Ti(CH_3)\{[OC(O)C_5H_4]Cr(CO)_2NO\}$	2023	1927	1693		1642	1322
10	$Cp_2Ti(CH_3)\{[OC(O)C_5H_4]Cr(NO)_2Cl\}$			1822	1700	1640	1327
11	$Cp_2Ti(CH_3)\{[OC(O)C_5H_4]Cr(NO)_2I\}$			1817	1703	1646	1320
12	$Cp_2Ti(CH_3)\{[OC(O)C_5H_4]W(CO)_3CH_3\}$	2011	1918			1646	1313
13	$Cp_2Ti[(OC(O)C_5H_4)Cr(CO)_2NO]_2$	2017	1947	1704		1630	1303
14	$Cp_2Ti[(OC(O)C_5H_4)Cr(NO)_2Cl]_2$			1811	1712	1636	1308
15	$Cp_2Ti[(OC(O)C_5H4)Cr(NO)_2I]_2$			1818	1705	1646	1318
16	$Cp_2Ti[(OC(O)C_5H_4)W(CO)_3CH_3]_2$	2016	1917			1635	1300
	$Cp_2Ti[OC(O)H]_2$					1644	1290