

Synthesis and Structure of
[bis(η^5 -cyclopentadienyl)][bis(cynichrodеноato)]titanium
 $\text{Cp}_2\text{Ti}\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2\text{NO}\}_2$

Yu-Pin Wang^{*}, Su-Ru Pang, Hsiu-Yao Cheng, Tso-Shen Lin

Abstract

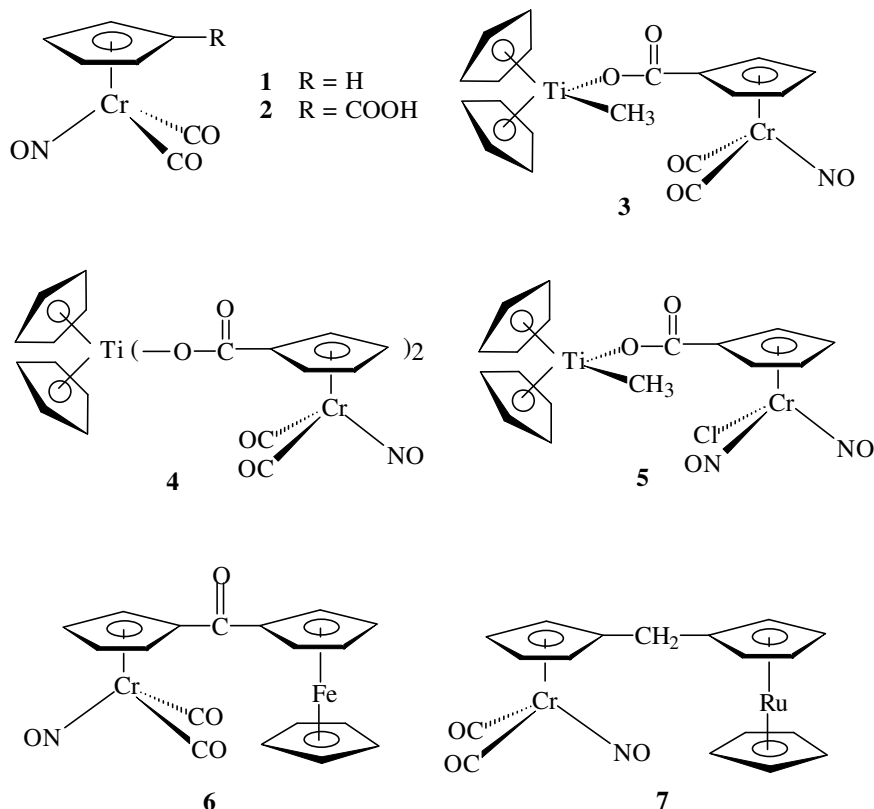
Complete demethylation of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ in dichloromethane with 2 molar equivalent of $[\eta^5\text{-(C}_5\text{H}_4\text{COOH)}]\text{Cr}(\text{CO})_2\text{NO}$ (**2**) gives $\text{Cp}_2\text{Ti}\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2\text{NO}\}_2$ (**4**). The structure of **4** has been solved by X-ray diffraction studies: space group, $P2_1/c$; monoclinic; $a = 15.740(5)$, $b = 7.2506(24)$, $c = 25.053(10)$ Å, $\beta = 108.16(3)^\circ$; $Z = 4$. In one of the cynichrodenyl moieties, the nitrosyl group is located at the site away from the exocyclic carbonyl carbon of the $\text{Cp}(\text{Cr})$ ring with twist angle of 177.11° . The exocyclic carbon is bent towards the chromium atom with a θ angle of 0.79° . The electron density distribution in the cyclopentadienyl ring of $\text{Cp}(\text{Cr})$, based on the ^{13}C NMR data, are compared with the calculations via density functional B3LYP correlation- exchange method.

Keywords: Cynichrodene, Titanocene, Nitrosyl, Carboxylate, B3LYP

1 Introduction

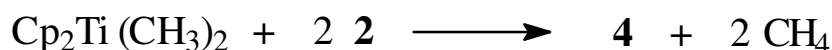
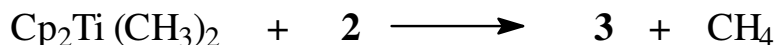
Functionally substituted derivatives of (η^5 -cyclopentadienyl) dicarbonylnitrosylchromium (**1**) (hereafter called cynichrodene) have been the subject of continuing interest in our laboratory. The opposite orientation between the NO ligand and the π -donor or the π -acceptor substituent on the Cp ring of monosubstituted cynichrodene derivatives was discovered [1]. The nitrosyl group is located at the side towards the π -donor substituent, while trans oriented to the π -acceptor substituent. The qualitative relationship of nonplanarity of Cp-exocyclic carbon to substituent π -donor or π -acceptor interactions have also been addressed. The 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. For π -acceptor substituents, approximately in the Cp plane or bent slightly toward the $\text{Cr}(\text{CO})_2\text{NO}$ fragments results. The magnitudes and directions of these distortions of the Cp planarity appear to be due primarily to electronic effects.

In hopes of confirming those hypotheses, as well as the potential ability of the early transition metal to activate a small molecule such as CO on the late transition metal centers[2] and the established antitumor or anti-inflammatory activities of titanocene carboxylates or titanocene dicarboxylates[3-5], have prompted us to synthesize complexes **3**[6] and **4**[7].



2 Results and discussion

Complex $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{OC}(\text{O})\text{C}_5\text{H}_4\}\text{Cr}(\text{CO})_2\text{NO}$ **3** was prepared through mono-demethylation of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ with 1 molar equivalent of **2** [6]. With 2 molar equivalent, complete demethylation of $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ gave complex $\text{Cp}_2\text{Ti}\{\text{OC}(\text{O})\text{C}_5\text{H}_4\}\text{Cr}(\text{CO})_2(\text{NO})\}_2$ **4**[7].



The unequivocal assignments of ^{13}C chemical shifts for **4**[7] and **5** [6] were correlated well with the density functional B3LYP calculations from the X-ray data of **4** and **5**[6]. The average charges of C(2,5) and C(3,4) are -0.1897 and -0.2486 (Table 1a) for **5**. For complex **4**, the corresponding charges are -0.2327 and -0.2580 for Cp(Cr1), and -0.2538 and -0.2547 for Cp(Cr2) (Table 1b). The much less difference between the average charges of C(2,5) and C(3,4) for **4** than those for **5** is conceivable due to the weaker electron-withdrawing property of $(\text{CO})_2(\text{NO})$, compared to that of $(\text{NO})_2\text{Cl}$.

The molecular structure of **4** is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The atomic coordinates of the atoms are listed in Table 3. For the purpose of comparison, selected structural data of **4**, **5**, $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3$ and $\text{Cp}_2\text{Ti}\{\text{OC}(\text{O})\text{C}_5\text{H}_4\}\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ are listed in Table 4; those of **1**, **4**, **6** and **7** are listed in Table 5. The molecular structure of **4** shows monodentate attachments of each carboxylate group to the small titanium metal, a usual feature for the carboxylate complexes of titanocene due to the steric crowdedness around the small titanium metal center. The Ti-O distance of 1.916(3) and 1.942(3) in **4** is comparable with those found in $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3$ (1.940(3) Å) [8] and $\text{Cp}_2\text{Ti}\{\text{OC}(\text{O})\text{C}_5\text{H}_4\}\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ (1.923 and 1.972 Å) [9], however, it is slightly shorter than those in **5** (1.977(2) Å) (Fig. 2) [6]. The angles of Ti-O-C(O) were also compared. Angles of 149.7(3) and 142.2(3)° in **4** are comparable with those found in $\text{Cp}_2\text{Ti}(\text{CH}_3)\{\text{OC}(\text{O})\text{C}_6\text{H}_5\}\text{Cr}(\text{CO})_3$ (149.6°) [8] and $\text{Cp}_2\text{Ti}\{\text{OC}(\text{O})\text{C}_5\text{H}_4\}\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}_6\text{H}_5)_2$ (139.4 and 148°) [9]. However, the angles are larger than those in **5** (137.1(2)).

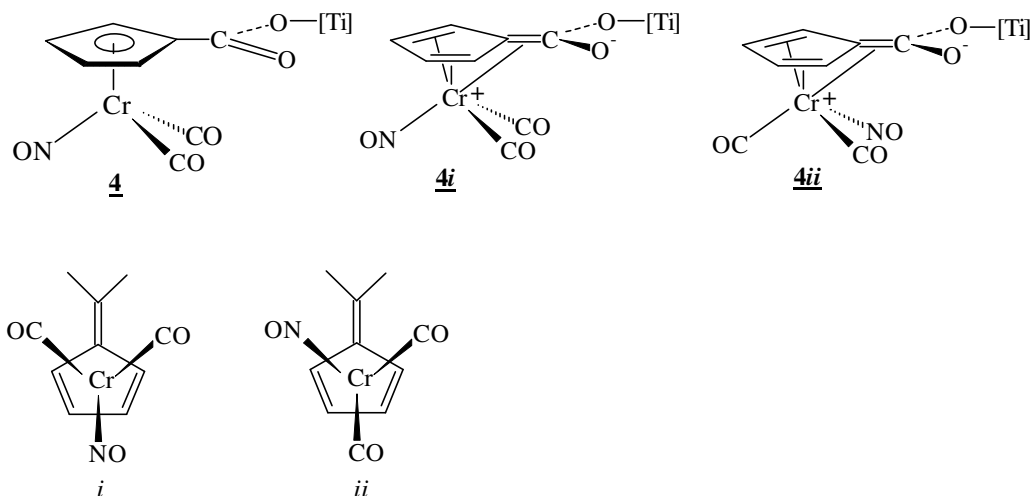
Comparatively, the shorter Ti-O distance and the relatively larger Ti-O-C angle indicate the greater extent of Ti-O π -bonding in **4**, than those in **5**. Which is conceivable due to the greater extent of electron donating from the less electron-deficient $\text{CpCr}(\text{CO})_2(\text{NO})$ moiety, compared to $\text{CpCr}(\text{NO})_2\text{Cl}$ moiety, to the carboxylato oxygen, increasing π -donor

tendency of the oxygen to Ti atom. It entails that the noncoordinated oxygen atoms are farther away from titanium (3.70, 3.54 Å in **4** versus 3.47 Å in **5**).

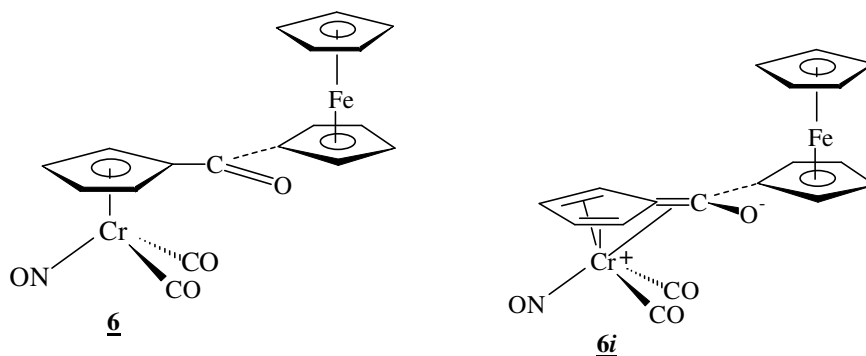
The bond angles of the carboxylate C-C(O)-O groups are non-equivalent, the largest angle of 125.5(4) (O(1)-C(16)-O(2)) and 126.2° (O(3)-C(26)-O(4)), respectively, in each of the carboxylate groups may be caused by the steric interference between the two oxygen atoms and Cp(Ti) rings. The Ti-Cp(centroid) distances (2.047, 2.058 Å) and the Cp(centroid)-Ti-Cp(centroid) angle (131.74°) are normal, compared with those values of the carboxylate complexes of titanocene (2.040-2.063 Å; 131.7-134.8°) [10].

For CpCr(CO)₂NO moiety of **4**, several important features are observed. The coordination geometry about each of Cr centers is approximately a distorted tetrahedron with two carbonyl groups, the Cp group and nitrosyl group as the four coordination sites. The nitrosyl group of Cp(Cr1) cynichrodenyl moiety is located at the site away the exocyclic of carbon of Cp(Cr1) ring with a twist of 177.11°, while in the Cp(Cr2) cynichrodenyl fragment, the nitrosyl group is located at the site toward the exocyclic carbon of the Cp(Cr2) ring with a twist angle of 93.40°. The twist angle is defined as the torsional angle between the nitrogen atom, the Cr atom, the Cp ring center and the ring carbon atom bearing the exocyclic carbon.

In the case of Cp(Cr1) cynichrodenyl moiety, the preference for the symmetrical isomer *i* to the unsymmetrical 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 trans to the better π -accepting ligand, i.e. NO⁺. As a result, the exocyclic carbon is slightly bent towards the chromium atom with θ angle of 0.79°.



The θ angle is defined as the angle between the exocyclic C-C bond (C(11)-C(16)) and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal. The exocyclic C-C bond of 1.489(6) Å [C(11)-C(16)] in the case of Cp(Cr1), is slightly shorter than that of **7** (1.502(11) Å) [1], but is longer than that found in **6** [11] (1.477(5) Å) (Fig. 3). The smaller contribution of canonical form **4i** than **6i** to each



of the corresponding structures **4** and **6** may explain such behavior. This phenomenon is conceivable, since Cp₂Ti is an electron donating group, the resonance between the two carboxylate oxygens overwhelming the resonance contribution of canonical form **4i** to **4**. The smaller contribution of **4i** to **4** leads to longer exocyclic bond length of C(11)-C(16).

It is interesting to find the differences between the two cynichrodene moieties, Cp(Cr1) and Cp(Cr2) in **4**. In the case of Cp(Cr2), the long exocyclic C-C bond (1.495(7) Å [C(21)-C(26)]), the smaller twist angle (93.4°), and the negative θ value (-0.52°) indicate the lack of resonance contribution of either canonical form *i* or *ii*, as in the case of methylene substituted cynichrodenyl moiety of **7** (1.502(11)Å; 24.4°; -0.69°). The steric crowdedness may account for the different configurations. The dihedral angle between the two Cp(Cr)s is 33.10° and both Cr(CO)₂(NO) moieties are pointed to the same direction, a cisoid conformation, geometrically. The Cr-N-O angles of 177.7(4) and 179.6(5)°, a linear M-NO linkage, are not significantly different from 179.4(3)° in **6** [11] and 174.7(7)° in **7** [1]. The steric effect may also reflect on the dihedral angle, 10.7° for Cp(Cr1) and 8.31° for Cp(Cr2), deviating from the zero degree of coplanarity, between the carbonyl plane and the corresponding Cp(Cr).

3 Experimental

3.1 Preparation of [bis(η^5 -cyclopentadienyl)][bis(cynichrodenoato)] titanium **4**

As this product is light sensitive, all operations were carried out with the exclusion of light. To a solution of dicarbonyl(η^5 -carboxycyclopentadienyl)nitrosylchromium **2** (1.00g, 4.05 mmol) in 80 ml of dichloromethane, bis(η^5 -cyclopentadienyl)dimethyltitanium (0.38 g, 1.83 mmol) was added in an ice bath. The resulting solution was stirred at 0°C for 4 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)][bis(cynichrodenoato)] titanium **4** (0.89 g, (73 %); d.p., 206°C) was obtained after vacuum drying. An analytical sample (an orange gleamy needle) was prepared by recrystallization using the solvent expansion method from dichloromethane: n-hexane(1:2) at 0°C for 48 h.

3.2. X-ray Diffraction analysis of **4**

The intensity data were collected on a Nonius diffractometer with a graphite monochromator (Mo-K α radiation). θ -2 θ scan data were collected at room temperature (25°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* [12]. All calculations were performed on a PC computer using Shelex software package [13].

3.3 Computational Method

In this study, we use the B3LYP hybrid method involving the three-parameter Becke exchange functional [14] and a Lee-Yang-Parr correlation functional [15]. All calculations are performed with the Gaussian-03 program using the 6-311G(d,p) basis set [16]. The geometries for **4** 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 [17]. An important feature of the NBO method is that the presence of diffuse functions in the basis sets does not affect the results.

Acknowledgements

The authors are grateful to the National Science Council of Taiwan (NSC-90-2113-M-029-016) for kindly support of this research program and the computational resources provided by National Center for High-Performance Computing (NCHC).

References

- [1] Y.-P. Wang, Pauling Wu, H.-Y. Cheng, T.-S. Lin, S.-L. Wang, J. Organomet. Chem., 694 (2009) 285.
- [2] T. T. Nadasdi and D. W. Stephan, Coord. Chem. Rev., 147 (1996) 147.
- [3] A. Prokop, A. Selig, A. Gansaeuer and D. Franke, Ger. Offen. (2008) DE 102006054690 A1 20080521.
- [4] P. Koepf-Maier and H. Koepf, Anticancer Research 6 (1986) 227.
- [5] Z.-Z. Zeng, Chin. J. of Chem., 20 (2002) 474.
- [6] Y.-P. Wang, S.-R. Pang, H.-Y. Cheng, T.-S. Lin, Y. Wang, G.-H. Lee, J. Organomet. Chem., 693 (2008) 329.
- [7] Y.-P. Wang, S.-R. Pang, T.-S. Lin, J. Organomet. Chem., 696 (2011) 2065.
- [8] H.-M. Gau, C.-T. Chen, T.-T. Jong and M.-Y. Chein, J. Organomet. Chem., 448 (1993) 99.
- [9] H.-M. Gau, C.-C. Schei, L.-K. Liu and L.-H. Luh, J. Organomet. Chem., 435 (1992) 43.
- [10] J. S. Merola, K. S. Campo, R. A. Gentile and M. A. Modrick, Inorg. Chim. Acta, 165 (1989) 87.
- [11] Y.-P. Wang, J.-M. Hwu, S.-L. Wang J. Organomet. Chem., 371 (1989) 71.
- [12] International Tables for X-ray Crystallography, Kynoch, Birmingham, UK, Vol. IV, 1974.
- [13] E.J. Gabe, Y. LePage, J.-P. Charland, F. L. Lee, P.S. White, J. Appl. Crystallogr., 22 (1989) 384.
- [14] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [15] C. Lee, W. Yang and R.G Parr, Phys. Rev. B., 37 (1988) 785.
- [16] 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.

[17] A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, 88(6) (1988) 899.

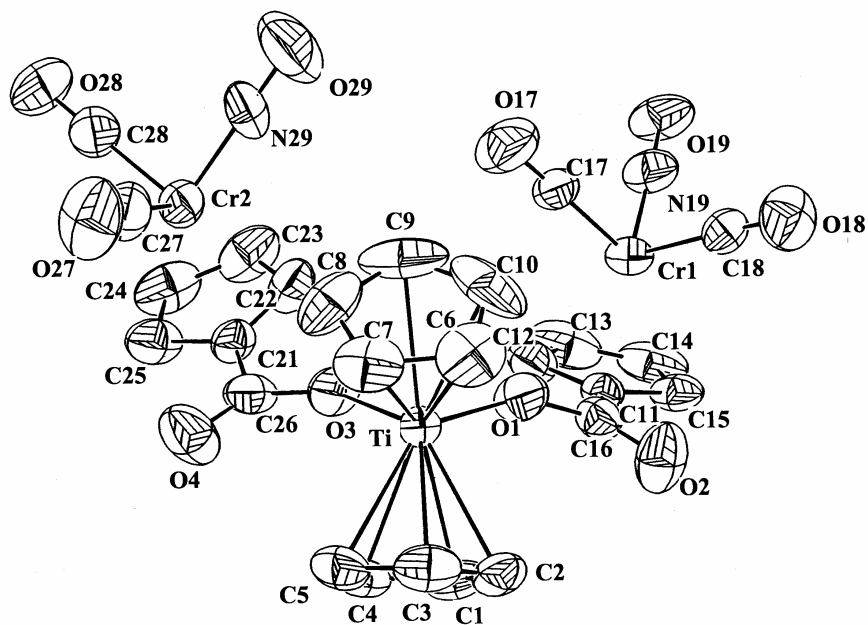


Fig. 1. ORTEP drawing of molecule 4

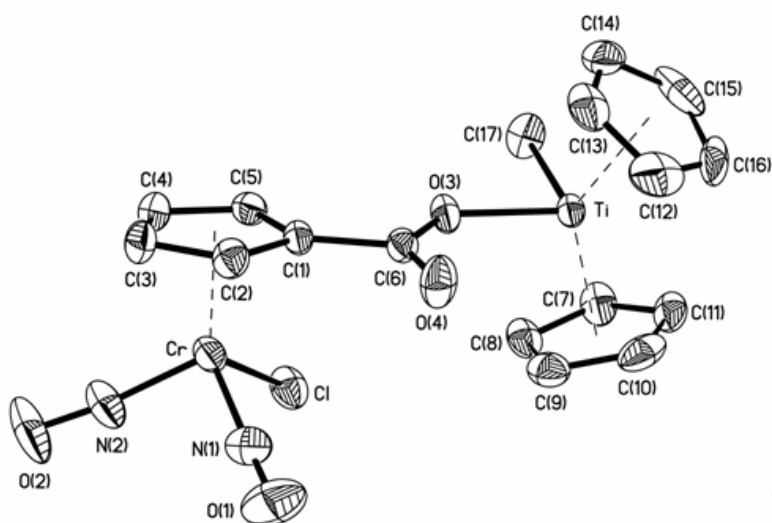


Fig. 2. ORTEP drawing of of 5

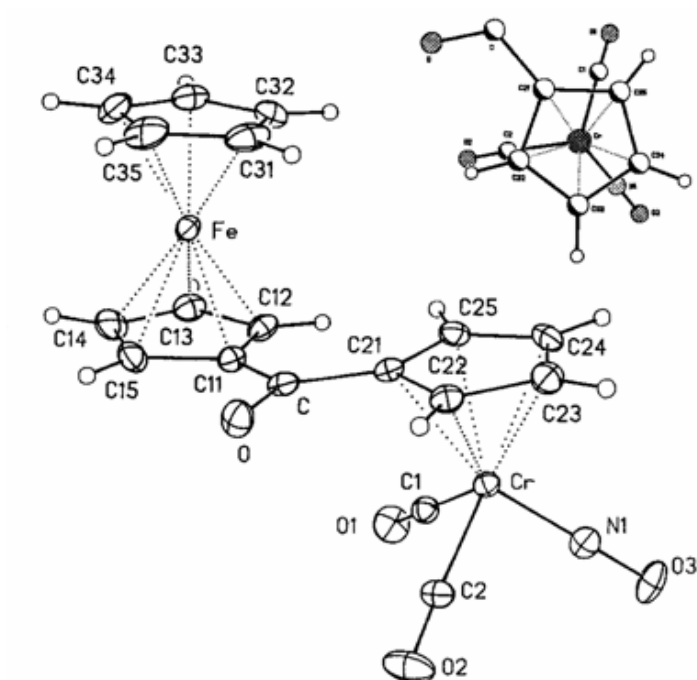


Fig. 3. ORTEP drawing of molecule **6** with the view along the normal of Cp(Cr) ring

Table 1a

Selected net atomic charges for **5** using the 6-311G(d,p) basis set

C(1) -0.21522 C(2) -0.20158 C(3) -0.23829 C(4) -0.25887 C(5) -0.17778

Table 1b

Selected net atomic charges for **4** using the 6-311G(d,p) basis set

Cp(Cr1)

C(11) -0.23511 C(12) -0.23697 C(13) -0.26406 C(14) -0.25184 C(15) -0.22843

Cp(Cr2)

C(21) -0.20538 C(22) -0.24058 C(23) -0.27771 C(24) -0.23168 C(25) -0.26704

Table 2Selected bond length (Å) and selected bond angles (°) for **4**

C(1)-C(2)	1.394(7)	C(6)-C(7)	1.395(9)
C(1)-C(5)	1.373(7)	C(6)-C(10)	1.375(11)
C(2)-C(3)	1.382(8)	C(7)-C(8)	1.366(9)
C(3)-C(4)	1.393(7)	C(8)-C(9)	1.364(11)
C(4)-C(5)	1.385(7)	C(9)-C(10)	1.352(12)
C(11)-C(12)	1.419(7)	C(21)-C(22)	1.406(7)
C(11)-C(15)	1.405(6)	C(21)-C(25)	1.417(6)
C(12)-C(13)	1.399(8)	C(22)-C(23)	1.404(8)
C(13)-C(14)	1.411(10)	C(23)-C(24)	1.383(9)
C(14)-C(15)	1.399(8)	C(24)-C(25)	1.391(8)
Cr1-C(17)	1.793(5)	Cr2-C(27)	1.807(5)
Cr1-C(18)	1.844(5)	Cr2-C(28)	1.823(5)
Cr1-N(19)	1.763(4)	Cr2-N(29)	1.754(5)
C(17)-O(17)	1.145(6)	C(27)-O(27)	1.144(6)
C(18)-O(18)	1.138(6)	C(28)-O(28)	1.156(6)
N(19)-O(19)	1.171(5)	N(29)-O(29)	1.154(6)
C(16)-O(1)	1.299(5)	C(26)-O(3)	1.284(6)
C(16)-O(2)	1.197(6)	C(26)-O(4)	1.202(6)
C(16)-C(11)	1.489(6)	C(26)-C(21)	1.495(7)
Cr1-cen.(Cp(Cr1))	1.836	Cr2-cen.(Cp(Cr2))	1.847
Cr1-----C(16)	3.219	Cr2-----C(26)	3.240
Cr1---C(Cp(Cr1)) ave.	2.192	Cr2---C(Cp(Cr2)) ave.	2.197
Ti-C(1)	2.371(4)	Ti-O(1)	1.916(3)
Ti-C(2)	2.363(4)	Ti-O(3)	1.942(3)
Ti-C(3)	2.360(4)	Ti....O(2)	3.696
Ti-C(4)	2.345(4)	Ti....O(4)	3.541
Ti-C(5)	2.373(4)	Cp1..Ti	2.0562
Ti-C(6)	2.325(5)	Cp2..Ti	2.0615
Ti-C(7)	2.353(5)	Ti----cen.(Cp1)	2.047
Ti-C(8)	2.391(5)	Ti----cen.(Cp2)	2.058

Ti-C(9)	2.388(5)		
Ti-C(10)	2.370(5)		
C(17)-Cr1-C(18)	93.01(20)	C(27)-Cr2-C(28)	93.14(20)
C(17)-Cr1-N(19)	93.75(18)	C(27)-Cr2-N(29)	92.99(23)
C(18)-Cr1-N(19)	95.00(19)	C(28)-Cr2-N(29)	92.49(22)
Cr1-C(17)-O(17)	178.8(4)	Cr2-C(27)-O(27)	178.4(4)
Cr1-C(18)-O(18)	178.0(4)	Cr2-C(28)-O(28)	179.6(4)
Cr1-N(19)-O(19)	177.7(4)	Cr2-N(29)-O(29)	179.6(5)
C(12)-C(11)-C(16)	126.5(4)	C(22)-C(21)-C(26)	126.7(4)
C(15)-C(11)-C(16)	125.3(4)	C(25)-C(21)-C(26)	125.5(4)
O(1)-C(16)-O(2)	125.5(4)	O(3)-C(26)-O(4)	126.2(4)
O(1)-C(16)-C(11)	112.6(4)	O(3)-C(26)-C(21)	112.9(4)
O(2)-C(16)-C(11)	121.9(4)	O(4)-C(26)-C(21)	120.8(4)
Ti-O(1)-C(16)	149.7(3)	Ti-O(3)-C(26)	142.2(3)
cen.(Cp1)-Ti-cen.(Cp2)	131.74	O(1)-Ti-O(3)	90.69(13)
cen.(Cp1)-Ti-O(1)	107.55	cen.(Cp2)-Ti-O(1)	106.12
cen.(Cp1)-Ti-O(3)	108.86	cen.(Cp2)-Ti-O(3)	104.24

Dihedral angles between planes

Cp(Cr1)(cen.), Cr1, C(11) and Cp(Cr1)(cen.), Cr1, C(17)	59.38
Cp(Cr1)(cen.), Cr1, C(11) and Cp(Cr1)(cen.), Cr1, C(18)	55.95
Cp(Cr1)(cen.), Cr1, C(11) and Cp(Cr1)(cen.), Cr1, N(19)	177.11
Cp(Cr2)(cen.), Cr2, C(31) and Cp(Cr2)(cen.), Cr2, C(27)	29.92
Cp(Cr2)(cen.), Cr2, C(31) and Cp(Cr2)(cen.), Cr2, C(28)	93.40
Cp(Cr2)(cen.), Cr2, C(31) and Cp(Cr2)(cen.), Cr2, N(29)	147.31
Cp(Cr1) and carbonyl plane (C11, C16, O1, O2)	10.7
Cp(Cr2) and carbonyl plane (C21, C26, O3, O4)	8.31
Cp(Cr1) and Cp(Cr2)	33.10

Table 3Atomic Parameters x, y, z and Beq of **4**

E.S. Ds. Refer to th elast digit printed

	x	y	z	Beq
Ti	0.57991	0.64074	0.14057	2.64(4)
Cr(1)	0.84202	0.84284	0.04937	3.76(4)
Cr(2)	0.86667	0.84694	0.33075	4.19(4)
C(1)	0.4758	0.8635	0.08959	4.4(3)
C(2)	0.4442	0.6908	0.06788	4.5(3)
C(3)	0.4238	0.5938	0.1098	4.5(3)
C(4)	0.4447	0.7031	0.15787	4.3(3)
C(5)	0.4746	0.8708	0.14413	4.2(3)
C(6)	0.5729	0.3235	0.12636	5.8(3)
C(7)	0.5644	0.3522	0.1795	5.0(3)
C(8)	0.6436	0.4215	0.21334	5.9(3)
C(9)	0.7005	0.434	0.1821	7.1(4)
C(10)	0.6587	0.3724	0.1295	7.7(5)
O(1)	0.63915	0.7201	0.08838	4.91(17)
O(2)	0.58301	0.7183	-0.00463	6.12(20)
C(16)	0.6352	0.7732	0.03816	3.6(3)
C(11)	0.7036	0.9154	0.03845	3.19(22)
C(12)	0.7589	1.011	0.08608	4.5(3)
C(13)	0.8139	1.1296	0.0675	6.7(4)
C(14)	0.7932	1.1077	0.0089	6.1(4)
C(15)	0.7246	0.9773	-0.00905	4.11(25)
C(17)	0.8686	0.6925	0.10912	4.01(25)
O(17)	0.88406	0.5956	0.14703	7.19(24)
C(18)	0.8208	0.6493	-0.00085	3.80(24)
O(18)	0.80527	0.5319	-0.03259	6.29(23)
N(19)	0.9547	0.872	0.05252	5.15(23)
O(19)	1.02975	0.8962	0.05594	6.31(21)
O(3)	0.65446	0.8031	0.19787	4.69(16)
O(4)	0.61068	0.852	0.27268	6.66(22)
C26	0.6632	0.8681	0.24696	4.4(3)
C21	0.7488	0.9713	0.27134	3.85(23)
C22	0.8202	0.9831	0.24899	5.1(3)
C23	0.8867	1.0939	0.2852	6.4(3)
C24	0.8559	1.152	0.32839	6.2(3)
C25	0.7716	1.0777	0.32124	5.1(3)
C27	0.8021	0.6762	0.35383	5.3(3)
O27	0.7596	0.569	0.36736	8.1(3)
C28	0.9495	0.8664	0.40006	5.0(3)

O28	1.00236	0.8789	0.44391	6.98(22)
N29	0.9295	0.6796	0.30912	5.8(3)
O29	0.9704	0.5691	0.29465	10.2(3)
H1	0.495	0.974	0.07	4.7
H2	0.442	0.644	0.029	5.1
H3	0.395	0.466	0.104	4.7
H4	0.442	0.661	0.197	5.1
H5	0.491	0.985	0.169	4.8
H6	0.527	0.277	0.091	6.2
H7	0.508	0.327	0.19	5.5
H8	0.66	0.459	0.256	6.0
H9	0.765	0.479	0.194	6.7
H10	0.689	0.361	0.099	7.6
H12	0.76	0.987	0.128	5.3
H13	0.861	1.224	0.092	6.3
H14	0.823	1.181	-0.015	6.2
H15	0.694	0.935	-0.051	4.9
H22	0.823	0.918	0.212	5.5
H23	0.95	1.121	0.282	6.5
H24	0.888	1.242	0.359	6.2
H25	0.731	1.093	0.347	6.0

* Mean atoms with composite scattering factors ($2/3$ O + $1/3$ N)

Table 4
Selected structural data

Compound	Bond length (Å)			Bond angle(°)		
	Ti-O	Ti-----O	Ti-Cp (centroid)	Ti-O-C(O)	Cp1(centroid)-Ti-Cp2(centroid)	C-C(O)-O The largest angle
4 Cp ₂ Ti[(OC(O)C ₅ H ₄)Cr(CO) ₂ NO] ₂	1.916(3)	3.696	2.047	149.7(3)	131.74	125.5(4)
	1.942(3)	3.541	2.058	142.2(3)		126.2(4)
5 Cp ₂ Ti(CH ₃){[O-C(O)-C ₅ H ₄]Cr(NO) ₂ Cl}	1.977(2)	3.468	2.056	137.1(2)	132.78	126.1(3)
			2.061			
Cp ₂ Ti{[OC(O)C ₆ H ₅]Cr(CO) ₃ } ₂	1.940(3)		2.060	149.6	132.4	125.4(4)
			2.061			
Cp ₂ Ti{[(OC(O)C ₅ H ₄)Fe(CO) ₂ (CH ₂ C ₆ H ₅)] ₂	1.923	3.652	2.055	148.0	131.48	125.9
	1.972	3.528		139.4		126.0

Table 5Selected structural data of **1**, **4**, **6** and **7**^a

Compound	Bond length (Å)		$\omega\text{Cr}^{\text{b}(\circ)}$	$\theta\text{Cr}^{\text{c}(\circ)}$	$\theta\text{M}^{\text{c}(\circ)}$	Cr--- C(exocyclic)	Cr-NO	Cr-CO	N=O	C=O	Cr-N-O	Cr-C-O	Cr-cent.(Cp)
	C(Cp(Cr))- C(exocyclic)	C(Cp(M))- C(exocyclic) (M=Fe or Ru)											
1							1.782(4)	1.805(4)	1.162(5)	1.140(5)	179.0(3)	178.0(4)	1.842
								1.809(44)		1.142(5)		178.4(4)	
4 (Cr1)	1.489(6) (C11-C16)		177.11	0.79		3.219	1.763(4)	1.793(5)	1.171(5)	1.145(6)	177.7(4)	178.8(4)	1.836
							1.844(5)			1.138(6)		178.0(4)	
(Cr2)	1.495(7) (C21-C26)		93.40	-0.52		3.240	1.754(5)	1.807(5)	1.154(6)	1.144(6)	179.6(5)	178.4(4)	1.847
							1.823(5)			1.156(6)		179.6(4)	
6	1.477(5)	1.470(5)	177.2	1.06	5.09	3.223	1.712(4)	1.846(4)	1.178(5)	1.135(5)	179.4(3)	177.2(4)	1.846
								1.865(4)		1.136(5)		179.0(4)	
7	1.502(11)	1.511(14)	24.44	-0.69	-1.65	3.287	1.757(9)	1.775(12)	1.174(12)	1.127(15)	174.7(7)	177.8(11)	1.830

^a **1** CpCr(CO)₂(NO)**4** Cp₂Ti[(OC(O)C₅H₄)Cr(CO)₂NO]₂**6** (CO)₂(NO)Cr[(η^5 -C₅H₄)-C(O)-(η^5 -C₅H₄)]FeCp**7** (CO)₂(NO)Cr[(η^5 -C₅H₄)-CH₂-(η^5 -C₅H₄)]RuCp^b $\omega\text{Cr}^{\text{b}(\circ)}$: the twist angle is defined as the torsional angle between the nitrosyl nitrogen atom, the chromium atom, the Cp center and the ring " carbon atom bearing the exocyclic carbon atom.^c $\theta\text{Cr}^{\text{c}(\circ)}$: the θ angle is defined as the angle between the exocyclic C-C bond and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal.

Table 6Selected crystal data and refinement parameters for **4**

Empirical formula	C ₂₆ H ₁₈ Cr ₂ N ₂ O ₁₀ Ti	
Formula weight	670.31	
Temperature	298°K	
Wavelength	0.70930 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.740(5) Å	= 90°
	b = 7.2506(24) Å	= 108.16(3)°
	c = 25.053(10) Å	= 90°
Volume	2716.7(16) Å ³	
Z	4	
Density (calculated)	1.664Mg/m ³	
Absorption coefficient	1.157 mm ⁻¹	
F(000)	1588	
Crystal size	0.50 x 0.50 x 0.55 mm ³	
Theta range for data collection	2.24 to 22.50°	
Index ranges	-16<=h<=16, 0<=k<=7, 0<=l<=26	
Reflections collected	3527	
Independent reflections	3527	
Completeness to theta =22.5°	99.9%	
Absorption correction	Psi-scan	
Max. and min. transmission	0.7607 and 0.5953	
Refinement method	Fullmatrix leastsquares on F ²	
Data / restraints /parameters	3527 / 0 / 371	
Goodness-of fit on F ²	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1243	
R indices (all data)	R1 = 0.0746, 2R2 = 0.1389	
Largest diff. peak and hole	0.290and -0.360 e.Å ⁻³	

化合物 $\text{Cp}_2\text{Ti}\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2\text{NO}\}_2$ 的合成及其結構分析

王玉蘋*, 潘淑如, 鄭秀瑤, 林哲生

摘 要

化合物 $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ 以二當量的化合物 $(\text{CO})_2(\text{NO})\text{Cr}[\eta^5-(\text{C}_5\text{H}_4-\text{COOH})]$ (**2**) 在二氯甲烷溶劑中去甲基化得化合物 $\text{Cp}_2\text{Ti}\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2(\text{NO})\}_2$ (**4**)。 **4** 的結構已由 X-ray 繞射法解析出。晶體參數如下：Space group, $P2_1/c$; monoclinic; $a = 15.740(5)$, $b = 7.2506(24)$, $c = 25.053(10)$ Å, $\beta = 108.16(3)^\circ$; $Z = 4$ 。 化合物 **4** 的一個 cymenchrodenyl 的硝基與 Cp(Cr)環上羰取代基 呈反方向的位向。其 ω 角為 177.11° 此環上羰取代基的碳的位向為向著 Cr 原子，其 θ 角為 0.79° 。經由二維異核相對應 NMR 光譜儀，化合物 $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{CO})_2(\text{NO})\}$ **3**, 與 **4** 的 C(2)-C(5)的 ^{13}C 化學位移得以確認。文中以 B3LYP correlation- exchange 的理論計算法得出的電子密度分佈情形，其結果呼應由 C^{13} NMR 化學位移所得之 Cp(Cr) 的電子密度分佈狀況。

關鍵字： $[\eta^5-(\text{環戊二烯})]$ 二羰亞硝基鉻；雙 $[\eta^5-(\text{環戊二烯})]$ 鈦；硝基；羧基；B3LYP