



Cyclopentadienyl chromium and tungsten complexes with halide, methyl and σ -phenylethynyl ligands: Structures of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{-C}\equiv\text{C-C}_6\text{H}_5)$, $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{I}$ and $[(\eta^5\text{-C}_5\text{H}_4)\text{-COOCH}_3]\text{W}(\text{CO})_3\text{Cl}$

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ABSTRACT

With copper(I) iodide as catalyst, σ -alkynyls, compounds $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C-C}_6\text{H}_5)$ (**5**), $[(\eta^5\text{-C}_5\text{H}_4)\text{-COOCH}_3]\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C-C}_6\text{H}_5)$ (**10**), and $[(\eta^5\text{-C}_5\text{H}_4)\text{-COOCH}_3]\text{W}(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_5)$ (**13**), were prepared from their corresponding metal chloride **1**, **6** and **12**. Structures of compound **3**, **5** and **12** have been solved by X-ray diffraction studies. In the case of **5**, there is an internal mirror plane passing through the phenylethynyl ligand and bisecting the Cp ring. The phenyl group is oriented perpendicularly to the Cp with an eclipsed conformation. The twist angle is 0° and 118.4° for $\text{-C}\equiv\text{C-Ph}$ and two NO ligands, respectively. The orientation is rationalized in terms of orbital overlap between ψ_3 of Cp, $d\pi$ of Cr atom, and π^* of alkynyl ligand, and complemented by molecular orbital calculation. The opposite correlation was observed on the chemical shift assignments of C(2)–C(5) on Cp ring in compounds **6** and **12**, using HetCOR NMR spectroscopy. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data and compared with the calculations via density functional B3LYP correlation-exchange method.

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1. Introduction

Chemistry associated with the cyclopentadienyl ring of three or four-legged piano stool Cp-complexes has been hampered because of the inability of these complexes to undergo electrophilic aromatic substitution. The number of isolated and well characterized Cp-functionally substituted chlorochromium, methylchromium, chlorotungsten and methyltungsten complexes are relatively small. In the case of $\text{CpCr}(\text{NO})_2\text{Cl}$ (**1**), only three complexes, $(\text{C}_5\text{H}_4\text{COOCH}_3)\text{Cr}(\text{NO})_2\text{Cl}$ (**6**) [1], $(\text{Fc-C}(\text{O})\text{-C}_5\text{H}_4)\text{Cr}(\text{NO})_2\text{Cl}$ [2], and $\text{Cp}_2\text{Ti}(\text{CH}_3)\{[\text{OC}(\text{O})\text{C}_5\text{H}_4]\text{Cr}(\text{NO})_2\text{Cl}\}$ [3] are reported in the literature. For the analogue of $\text{CpCr}(\text{NO})_2\text{CH}_3$ (**4**) there is only one, $(\text{C}_5\text{H}_4\text{COOCH}_3)\text{Cr}(\text{NO})_2\text{CH}_3$ [1], and for complex $\text{CpW}(\text{CO})_3\text{CH}_3$ there are 18 [4]. For Cp derivatives of compound $\text{CpCr}(\text{NO})_2(\text{C}\equiv\text{C-C}_6\text{H}_5)$ (**5**) and $\text{CpW}(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_5)$ [5], there are none.

The Cp–chromium complexes may have properties distinct from their iron analogues. Earlier [6], we reported the unequivocal assignments of C(2,5) and C(3,4) on the Cp ring of the (cyclopentadienyl)dicarbonylnitrosylchromium (hereafter called cynichrodene) derivatives bearing electron-withdrawing substituents in ^{13}C NMR spectra. The opposite correlation on the assignments between ferrocene and cynichrodene was a surprising finding. In

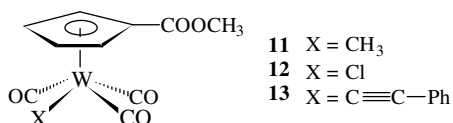
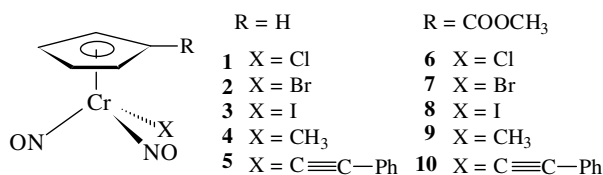
the case of ferrocene [7], the 3,4-positions are more sensitive to the electron-withdrawing substituent, while in the case of cynichrodene, the 2,5-positions are more sensitive to the electron-withdrawing substituent. The overall electron-withdrawing property of CO and NO ligands may exert the difference. The qualitative relationship of nonplanarity of Cp-exocyclic carbon to substituent π -donor and 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 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 [6]. In hope of confirming those hypotheses and extending those hypotheses to the $\text{W}(\text{CO})_3\text{Cl}$ analog, some Cp-functionally substituted metallocenes, containing $\text{Cr}(\text{NO})_2\text{Cl}$, $\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C-C}_6\text{H}_5)$, $\text{W}(\text{CO})_3\text{Cl}$ and $\text{W}(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_5)$ were studied. The exploration of the metal acetylides came from the impetus that those complexes evince interest in several perspectives: as useful precursors for preparation of organometallic polymers [8], as components in NLO (nonlinear optical) materials [9], molecular wires, light harvesting devices, molecular magnets, and liquid crystalline materials [10].

Herein, we report thorough spectral studies on **1–13**, and the crystal structures of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{I}$ (**3**), $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2$

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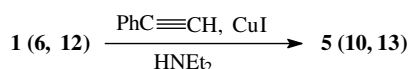
($-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$) (**5**) and $[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{W}(\text{CO})_3\text{Cl}]$ (**13**). Chromium dinitrosyl metallobenes with a σ -alkynyl ligand has never been reported in the literature and compound **5** appears to be the first Cr- σ -alkynyl of $\text{CpCr}(\text{NO})_2\text{R}$ complexes with X-ray confirmed structure.



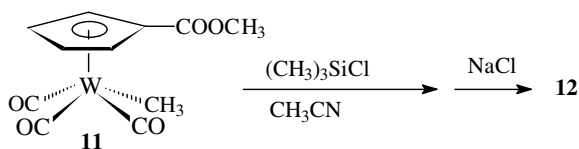
2. Results and discussion

2.1. Synthesis and characterization

Copper(I)-iodide-catalyzed reactions [11] were used to synthesize compounds **5**, **10** and **13**, transition metal σ -alkynyls, in yield of 42%, 38% and 74%, respectively, from corresponding metal chloride **1**, **6** and **12**. Presumably, through a copper(I) alkynyl intermediate, which then transfer the σ -alkynyl group to chromium or tungsten.



Compound **12** used in the preparation of **13**, was synthesized from $(\eta^5\text{-carbomethoxycyclopentadienyl})\text{tricarboxylmethyltungsten}$ (**11**) [12] by treating it with chlorotrimethylsilane in acetonitrile, presumably led to $[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{W}(\text{CO})_3(\text{CH}_3\text{CN})]^+\text{Cl}^-$. Reacting the resulting salt with sodium chloride gave **12**, in yield of 70%.



All compounds **1–10** exhibit two terminal nitrosyl stretching bands, the symmetric mode occurring at $1780\text{--}1829\text{ cm}^{-1}$ and the asymmetric mode at $1675\text{--}1732\text{ cm}^{-1}$ (Table 1).

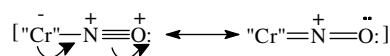
The absorption of organic carbonyl group of **6–10** is obscured by the asymmetric NO stretching band. The following order of increasing wavenumbers of symmetric NO stretching was observed: **4** (1780 cm^{-1}) < **5** (1805 cm^{-1}) < **3** (1808 cm^{-1}) < **2** (1820 cm^{-1}) < **1** (1823 cm^{-1}) for Cp-H derivatives and **9** (1789 cm^{-1}) < **8**

Table 1
IR spectra of **1–10**

		$\nu(\text{NO})$	
1	$\text{CpCr}(\text{NO})_2\text{Cl}$	1823	1715
2	$\text{CpCr}(\text{NO})_2\text{Br}$	1820	1705
3	$\text{CpCr}(\text{NO})_2\text{I}$	1808	1709
4	$\text{CpCr}(\text{NO})_2\text{CH}_3$	1780	1675
5	$\text{CpCr}(\text{NO})_2(\text{C}\equiv\text{C}-\text{Ph})$	1805	1689
6	$[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2\text{Cl}]$	1829	1732 ^a
7	$[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2\text{Br}]$	1826	1731 ^a
8	$[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2\text{I}]$	1821	1729 ^a
9	$[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2\text{CH}_3]$	1789	1723 ^a
10	$[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C}-\text{Ph})]$	1825	1724 ^a

^a The asymmetric NO stretching band is obscured by the organic carbonyl group ($-\text{COOCH}_3$).

(1821 cm^{-1}) < **10** (1825 cm^{-1}) < **7** (1826 cm^{-1}) < **6** (1829 cm^{-1}) for Cp-COOCH₃ derivatives. This trend is correlated well with the order of increasing tendency of electron-withdrawing property of a coordinated ligand on the chromium atom: $-\text{CH}_3 < -\text{I} \sim -\text{C}\equiv\text{C}-\text{Ph} < -\text{Br} < -\text{Cl}$. An electron-withdrawing ligand reduces the π back-bonding from Cr $d\pi$ -orbitals to the π^* orbitals of NO groups, and higher wavenumbers result. The symmetric nitrosyl stretching bands of compounds **6–10** were observed higher frequencies by $\sim 6\text{--}20$ wave numbers, compared with the corresponding bands of each unsubstituted parent compounds **1–5**. The electron-withdrawing substituent, carbomethoxy group, on Cp ring depletes the electron density of Cr, decreasing the tendency of π back-bonding from Cr to NO ligands, higher frequencies of NO result. Other functional groups of these compounds show their characteristic absorbances.



The ¹H and ¹³C NMR spectra for complexes **1–10** are listed in Tables 2 and 3 [7,13]. It is interesting to note that the same trend obtained in infrared spectra was also revealed. The order of increasing chemical shifts in ppm of Cp(Cr) protons and carbons were observed: **4** (5.40; 99.26) < **5** (5.68; 100.2) < **3** (5.73; 101.32) < **2** (5.72) < **1** (5.73; 103.02) in the Cp-H case (Since the ¹³C-spectroscopic data of **2** have never been reported in the literature, the data is not placed). And in the C₅H₄-COOCH₃ case, the order is: **9** (5.69, 101.16) < **10** (5.75, 101.19) < **8** (6.06, 103.30) < **7** (6.03, 104.06) < **6** (6.02, 105.10). Furthermore, the chemical shifts of protons and carbons on Cp(Cr) of **6–10** occur at lower field than those of their unsubstituted parent compounds **1–5**. The depletion of electron density of Cp(Cr) either by an electron-withdrawing coordinated ligand on the chromium atom or by the strong electron-withdrawing carbomethoxy substituent on the Cp ring is consistently revealed.

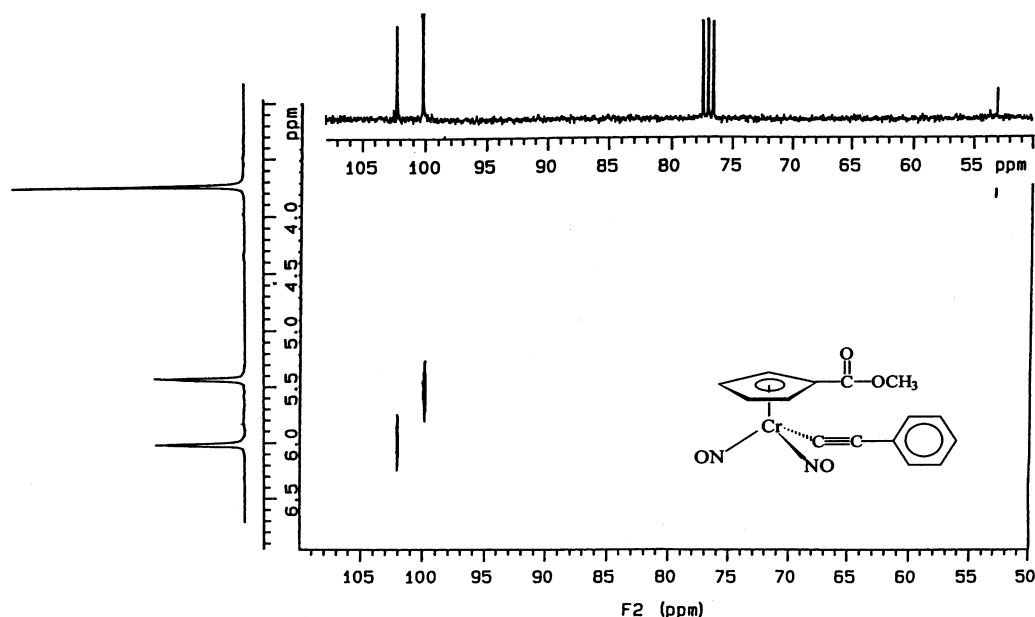
The assignments of ¹³C NMR spectra of **6–13** were based on standard ¹³C NMR correlation [3,13,14], 2D HetCOR, the DEPT technique and by comparison with other metallo-aromatic systems [15]. Figs. 1 and 2 displays the 2D ¹H{¹³C} HetCOR NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ (**10**) and $[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{W}(\text{CO})_3(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ (**13**), respectively. It is interesting to note the slopes of 2D spectra of compounds **10** and **13** are opposite, one is positive and the other one is negative. Accordingly, the unambiguous assignments were made: C(2,5) and C(3,4) of Cp(Cr) resonates at δ 102.37 and 100.01 for compound **10**, respectively; C(2,5) and C(3,4) of Cp(W) resonates at δ 91.91 and 95.47 for compound **13**, respectively. The assignment is a kind of surprise. In the case of $[(\eta^5\text{-C}_5\text{H}_4\text{-COOCH}_3)\text{Cr}(\text{NO})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)]$ (**10**), the 2,5 positions are more sensitive to the electron-withdrawing substituent,

Table 2
¹H NMR data

Compound	Cp(Cr)	Cp(Cr)		-OCH ₃
		H(2,5)	H(3,4)	
1	CpCr(NO) ₂ Cl		5.73 (s, 5)	
2	CpCr(NO) ₂ Br		5.72 (s, 5)	
3	CpCr(NO) ₂ I		5.73 (s, 5)	
4	CpCr(NO) ₂ CH ₃		5.40 (s, 5)	
5	CpCr(NO) ₂ (C≡C-Ph)		5.68 (s, 5)	
6	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ Cl	6.25 (t, 2)	5.78 (t, 2)	3.89 (s, 3)
7	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ Br	6.26 (t, 2)	5.79 (t, 2)	3.87 (s, 3)
8	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ I	6.29 (t, 2)	5.82 (t, 2)	3.85 (s, 3)
9	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ CH ₃	5.93 (t, 2)	5.44 (t, 2)	3.79 (s, 3)
10	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ (C≡C-Ph)	6.06 (t, 2)	5.43 (t, 2)	3.72 (s, 3)

Table 3
¹³C(1H) NMR data

Compound	Cp(Cr)	Cp(Cr)			C=O	-OCH ₃	Cr-CH ₃
		C(1)	C(2,5)	C(3,4)			
1	CpCr(NO) ₂ Cl		103.02 (C(1-5))				
3	CpCr(NO) ₂ I		101.32 (C(1-5))				
4	CpCr(NO) ₂ CH ₃		99.26 (C(1-5))				-1.22
5	CpCr(NO) ₂ (C≡C-Ph)		100.20 (C(1-5))				
6	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ Cl	103.14	106.05	104.14	161.87	52.79	
7	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ Br	102.56	105.56	103.65	161.99	52.82	
8	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ I	101.96	104.3	102.3	162.1	52.72	
9	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ CH ₃	101.78	102.83	99.48	163.65	52.08	0.85
10	[(η ⁵ -C ₅ H ₄)-COOCH ₃]Cr(NO) ₂ (C≡C-Ph)	102.54	102.37	100.01	160.68	53.01	

**Fig. 1.** 2D ¹H(¹³C) HetCOR NMR spectrum of **10** in CDCl₃.

while in the case of [(η⁵-C₅H₄)-COOCH₃]W(CO)₃(C≡C-C₆H₅) (**13**), the 3,4-positions are more sensitive to the electron-withdrawing substituent. In cyclopentadienyl chromium complexes (**6–10**), bearing a 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 [6]. However, for the same group VI metal, the opposite assignments were made for CpW(CO)₃X derivatives, **11** [3], **12** and **13**.

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 of the chromium atom. The weaker electron-withdrawing property of CO as compared with NO, may induce the greater extent of contribution of canonical form IIIi than IIi to each of the corresponding structures II and I. On a whole, these two factors 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)₃R derivatives [3] and those of ferrocenes derivatives [6], while the opposite correlation was observed for the derivatives of CpCr(NO)₂Cl (**1**) CpCr(NO)₂Br (**2**), CpCr(NO)₂I (**3**), and CpCr(NO)₂R [3,13].

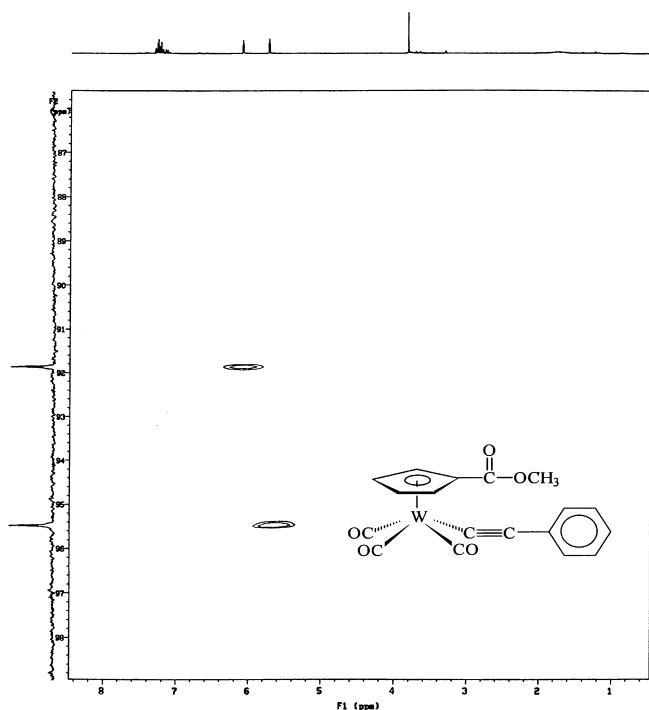
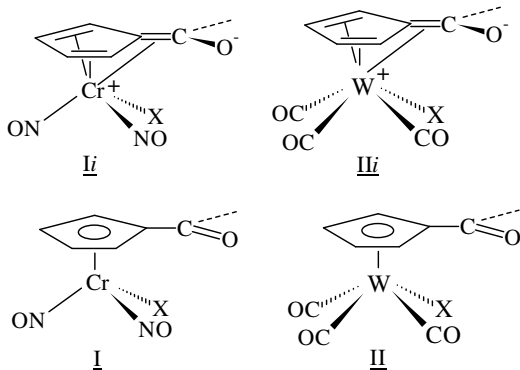


Fig. 2. 2D $^1\text{H}\{^{13}\text{C}\}$ HetCOR NMR spectrum of **13** in CDCl_3 .



A significant advantage of the ^{13}C NMR method over ^1H NMR spectroscopy is the relatively lower susceptibility of ^{13}C chemical shifts to the effects of magnetically anisotropic groups and ring current [16]. Therefore ^{13}C 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.

Unfortunately, neither of X-ray structures of **10** and **13** was obtained, the comparison between those of **6** and **12** was made instead. The unequivocal assignments of ^{13}C chemical shifts for **6** and **12** were correlated well with the ab initio calculations from the X-ray data of **6** and **12**. The average charges of C(2,5) and C(3,4) are -0.1593 and -0.2186 for compound **6**, and -0.2057 and -0.1711 for compound **12** (Table 4a).

With the fortune of obtaining the X-ray structures of both **3** and **5**, the comparison between the atomic net charges of those two compounds were studied via density functional B3LYP correlation-exchange method and compared with the data obtained from ^1H and ^{13}C NMR. The lower and higher field chemical shifts

Table 4a
Selected net atomic charges for **6** and **12** using the LANL2DZ basis set

	C(1)	C(2)	C(3)	C(4)	C(5)
6	-0.17459	-0.11286	-0.20274	-0.16865	-0.15037
12	-0.17983	-0.2205	-0.13291	-0.20932	-0.19095

Table 4b
Selected net atomic charges for **3** and **5** using the DGDZVP basis set

	C(1)	C(2)	C(3)	C(4)	C(5)
3	-0.23266	-0.24077	-0.19179	-0.23419	-0.20013
5	C(9)	C(10)	C(10A)	C(11)	C(11A)
	-0.18318	-0.24584	-0.24584	-0.22657	-0.22657

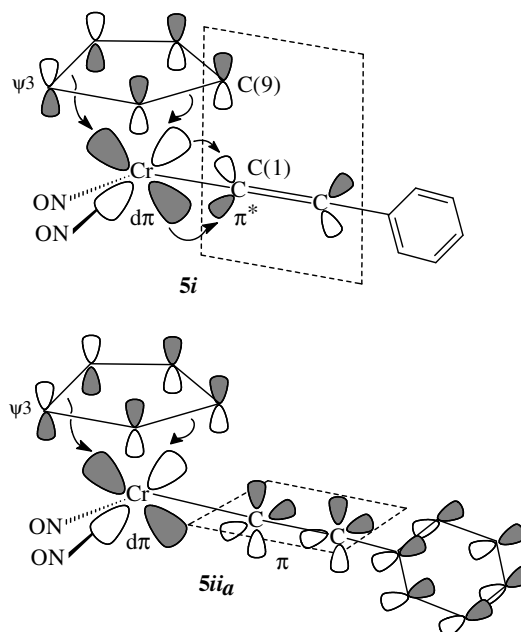
Table 4c
Selected net atomic charges for **5** using the DGDZVP basis set

C(3)	C(4) (o)	C(5) (m)	C(6) (p)	C(7) (m)	C(8) (o)
-0.07841	-0.1325	-0.14408	-0.17772	-0.14162	-0.13198

observed from **3** (δ 5.73; δ 101.32) and **5** (δ 5.68; δ 100.20) were correlated well with the data listed in Table 4b. The average charge of Cp-carbon is -0.2199 and -0.2256 for **3** and **5**, respectively. In the case of compound **5**, the electron-withdrawing inductive effect of alkynyl triple bond deshields the nearby *o*-carbon atoms to a greater extent than the more distant *m*- and *p*-positions, chemical shifts of δ 131.13 (*o*- C_6H_5), 127.94 (*m*- C_6H_5), and 125.94 (*p*- C_6H_5) ppm were obtained. The values were correlated well with the data listed in Table 4c. The average charge of *ortho*-, *meta*- and *para*- is -0.132 , -0.143 and -0.178 , respectively.

However, to discuss the chemical shifts of solution NMR spectra, optimized structures should be used for calculation of electron density (or atomic charge), instead of single point calculation based on the X-ray structure. Nonetheless, both complexes **3** and **5** crystallized in the same space group; large difference in crystal packing effects between them won't be anticipated. Unfortunately, at present we have no way of evaluating packing forces involved.

The molecular structures of **3**, **5** and **12** are shown in Figs. 3–5, respectively. Selected bond distances and angles are given in Tables 5–7.



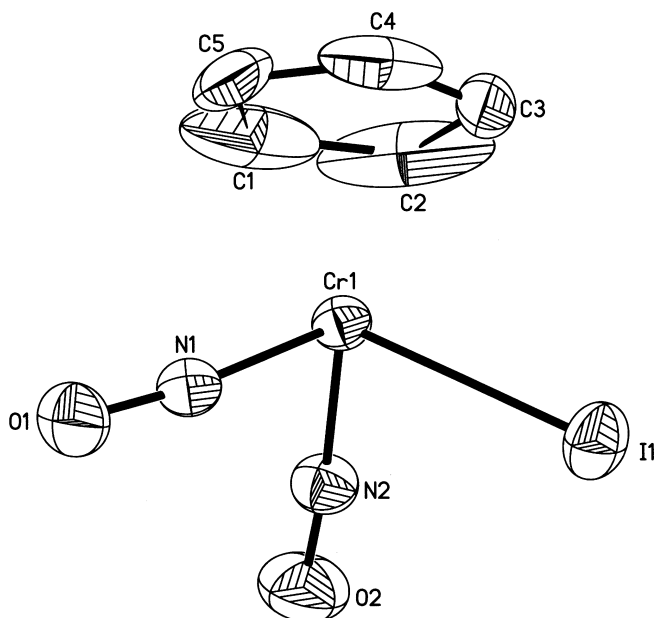


Fig. 3. Molecular configuration of 3.

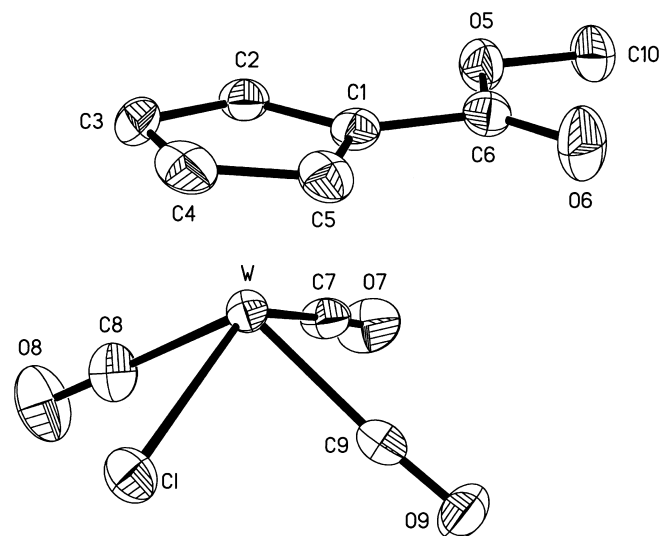
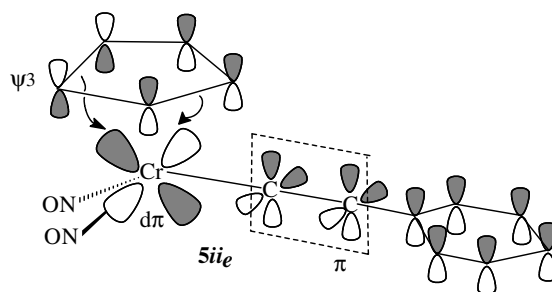


Fig. 5. Molecular configuration of 12.

In the case of **5**, the coordination geometry about the Cr center is approximately a distorted tetrahedron with two nitrosyl groups, the Cp group and phenylethynyl as the four coordination sites. There is a plane of symmetry passing through C(1)–Cr–C(9), and the phenylethynyl ligand is inlaid in the plane. The twist angle is 0° for $-\text{C}\equiv\text{C}-\text{Ph}$ ligand with respect to the plane of symmetry. The eclipsed and perpendicular orientations of phenyl group to the Cp ring is startling at the first glance. To achieve appropriate overlap between the corresponding orbitals might explain the preference. The electrons flow from ψ_3 orbital of Cp into the $d\pi$ of Cr, which in turn π -back donates electrons to the π^* orbital, perpendicular to Cp ring, on alkyne (**5i**). The electron density at both carbons of alkyne increases, which then delocalizes over the phenyl ring through resonance. Either perpendicular (**5ii_a**) or parallel orientation (**5ii_e**) of phenyl ring toward Cp ring would be anticipated.



The eclipsed orientation was also revealed by the corresponding bond lengths and bond angles. The bond length (1.408(6) in Å) of C(11)–C(11A), transoid to the alkyne ligand, is the longest among the five C–C bonds of Cp ring. And carbons C(11) and C(11A) were bent down to approach Cr and allowing Cp π orbital getting overlap with the $d\pi$ orbital of Cr. The shorter bond lengths in Å of Cr–C(11) (2.193(2)) and Cr–C(11A) (2.193(2)), and the longer bond length of Cr–C(9) (2.224(3)) were observed. As well, C(1) along

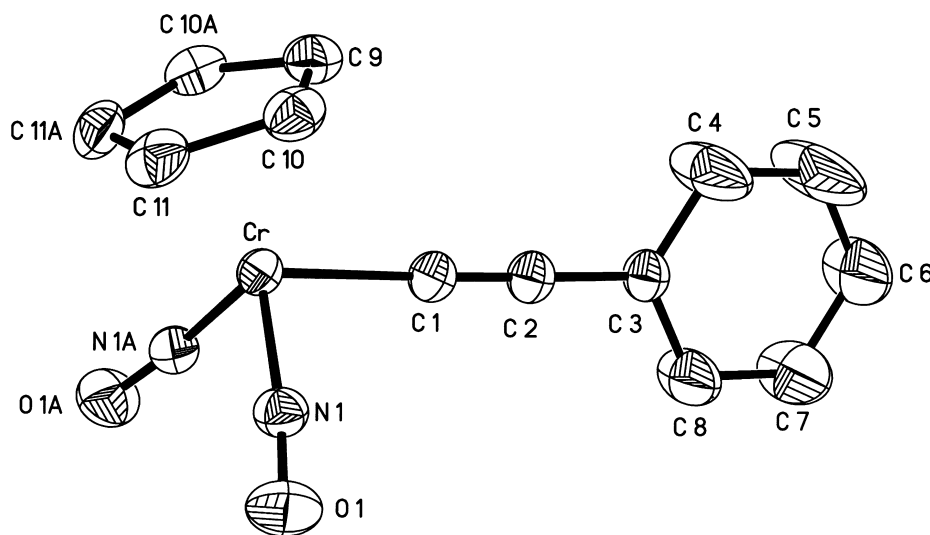


Fig. 4. Molecular configuration of 5.

Table 5
Selected bond length (Å) and selected bond angles (°) for **3**

Cr–C(1)	2.143(12)	
Cr–C(2)	2.140(12)	
Cr–C(3)	2.175(13)	
Cr–C(4)	2.200(11)	
Cr–C(5)	2.182(10)	
C(1)–C(2)	1.306(30)	
C(1)–C(5)	1.303(26)	
C(2)–C(3)	1.325(32)	
C(3)–C(4)	1.327(29)	
C(4)–C(5)	1.340(23)	
Cr–N(1)	1.7100(7)	
Cr–N(2)	1.708(6)	
Cr–I	2.673(2)	
N(1)–O(1)	1.156(10)	
N(2)–O(2)	1.168(10)	
Cr...Cp(cen.)	1.855	
O(1)...I	4.284	
O(2)...I	4.204	
N(1)–Cr–N(2)	95.3(3)	
N(1)–Cr–I	98.1(2)	
N(2)–Cr–I	96.3(2)	
Cr–N(1)–O(1)	171.7(5)	
Cr–N(2)–O(2)	174.7(5)	
Cp(cen.)–Cr–I	118.23	
Cp(cen.)–Cr–N(1)	120.89	
Cp(cen.)–Cr–N(2)	122.2	
Dihedral angles between planes		
Cp(cen.), Cr, I	and C(3), Cp(cen.), Cr	18.8
Cp(cen.), Cr, N(1)	and C(3), Cp(cen.), Cr	138.8
Cp(cen.), Cr, N(2)	and C(3), Cp(cen.), Cr	101.2

Table 6
Selected bond length (Å) and selected bond angles (°) for **5**

Cr–C(9)	2.224(3)	N(1A)–Cr–N(1)	94.89(13)
Cr–C(10)	2.211(2)	N(1A)–Cr–C(1)	97.56(9)
Cr–C(10A)	2.211(2)	N(1)–Cr–C(1)	97.56(9)
Cr–C(11)	2.193(2)	N(1A)–Cr–C(11A)	92.67(9)
Cr–C(11A)	2.193(2)	Cr–N(1)–O(1)	173.37(18)
C(9)–C(10)	1.399(3)	Cr–N(1A)–O(1A)	173.37(18)
C(9)–C(10A)	1.399(3)	Cr–C(1)–C(2)	178.9(3)
C(10)–C(11)	1.404(3)	C(1)–C(2)–C(3)	179.1(3)
C(11)–C(11A)	1.408(6)	C(2)–C(3)–C(4)	120.6(3)
C(10A)–C(11A)	1.404(3)	C(2)–C(3)–C(8)	122.1(3)
Cr–C(1)	2.013(3)	Cp(cen.)–Cr–C(1)	114.9
Cr–N(1A)	1.7126(19)	Cp(cen.)–Cr–N(1)	123.14
Cr–N(1)	1.7126(19)	Cp(cen.)–Cr–N(1A)	123.14
N(1)–O(1)	1.159(2)		
N(1A)–O(1A)	1.159(2)		
C(1)–C(2)	1.192(4)		
C(2)–C(3)	1.441(4)		
C(3)–C(4)	1.329(6)		
C(3)–C(8)	1.345(6)		
C(4)–C(5)	1.409(6)		
C(5)–C(6)	1.308(8)		
C(6)–C(7)	1.330(7)		
C(7)–C(8)	1.387(6)		
Cr...Cp(cen.)	1.856		
O(1)...C(1)	3.784		
O(1)...C(1A)	3.784		
Dihedral angles between planes			
Cp(cen.), Cr, C(1)	and C(9), Cp(cen.), Cr	0	
Cp(cen.), Cr, N(1)	and C(9), Cp(cen.), Cr	118.4	
Cp(cen.), Cr, N(2)	and C(9), Cp(cen.), Cr	118.4	

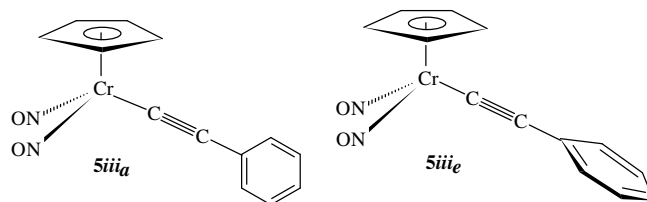
with the rest alkynyl group tilts up itself toward the Cp. The angle of Cp(cen.)–Cr–C(1) (114.90°) is small, relative to Cp(cen.)–Cr–N(1) (123.14°) and Cp(cen.)–Cr–N(2) (123.14°).

The bond length of Cr–ethynyl carbon(C(1)) (2.013(3) Å) is short, compared to 2.241(7) Å in complex Cr₃(dpa)₄(C≡C–Ph)₂

Table 7
Selected bond length (Å) and selected bond angles (°) for **12**

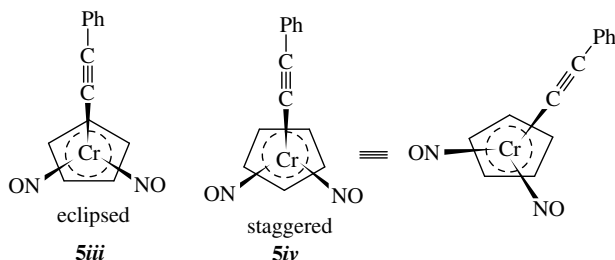
W–C(1)	2.264(7)	C(7)–W–C(9)	75.7(3)
W–C(2)	2.280(7)	C(7)–W–C(8)	77.0(3)
W–C(3)	2.372(7)	C(9)–W–C(8)	110.7(3)
W–C(4)	2.402(7)	C(7)–W–Cl	133.9(2)
W–C(5)	2.314(7)	C(8)–W–Cl	76.7(2)
C(1)–C(2)	1.409(10)	C(9)–W–Cl	79.2(2)
C(1)–C(5)	1.414(10)	W–C(7)–C(7)	178.0(6)
C(1)–C(6)	1.510(10)	W–C(8)–C(8)	179.2(8)
C(2)–C(3)	1.431(10)	W–C(9)–O(9)	175.6(6)
C(3)–C(4)	1.427(12)	Cp(cen.)–W–Cl	111.24
C(4)–C(5)	1.414(11)	Cp(cen.)–W–C(7)	114.86
W–C(7)	1.985(8)	Cp(cen.)–W–C(8)	124.55
W–C(8)	2.021(8)	Cp(cen.)–W–C(9)	124.70
W–C(9)	2.005(8)		
W–Cl	2.4889(17)		
C(7)–O(7)	1.153(9)		
C(8)–O(8)	1.124(9)		
C(9)–O(9)	1.131(9)		
C(6)–O(6)	1.187(8)		
C(6)–O(5)	1.331(8)		
C(10)–O(5)	1.439(8)		
W...Cp(cen.)	1.99		
O(7)...Cl	5.171		
O(8)...Cl	3.545		
O(9)...Cl	3.645		
Dihedral angles between planes			
Cp(cen.), W, Cl	and Cp(cen.), W, C(1)	141.13	
Cp(cen.), W, C(7)	and Cp(cen.), Cr, C(1)	39.35	
Cp(cen.), W, C(8)	and Cp(cen.), Cr, C(1)	130.50	
Cp(cen.), W, C(9)	and Cp(cen.), Cr, C(1)	49.99	
Cp(W) and carbonyl plane (C1, C6, O5, O6)		4.56	

(dpa = 2,2-dipyridylamide) [17]. Simple Cr⁰–C(sp³) single-bond distances are expected to fall in the range of 2.20–2.24 Å [18]. Allowing for the greater s character (and therefore shorter bond length) of the sp hybrid on alkynyl compared to the sp³ hybrid of the methyl group by about 0.07 Å we would expect the Cr⁰–C(sp) single-bond distance to be in the range of 2.13–2.17 Å [19]. Thus, the shorter ($\Delta = 0.12$ –0.16 Å) than expected Cr–C(1)(sp) distance demonstrates that there is an electron flow from Cr d π -orbitals to the π^* orbitals of alkynyl group, correlated well with the phenyl orientation observed in the X-ray structure. It is of interest to note that the difference ($\Delta = 0.128$ Å) between the bond lengths of M–C(sp) in **5** CpCr(NO)₂(C≡CPh) (2.013(3) Å) and those in *cis*-CpW(CO)₂(PET₃)(C≡CPh) (2.141(8) Å) is almost identical to the difference ($\Delta = 0.129$ Å) between those in Cr(CO)₆ (1.915 Å) [20] and W(CO)₆ (2.044 Å) [21], indicating the same kind of d π -back bonding from the metal to the π^* of alkynyl and CO ligands.



Curiosity aroused by the startling perpendicular orientation of phenyl ring toward the Cp(Cr) ring, we calculated the rotational barrier (0.90 kcal mol⁻¹) of phenyl ring with respect to Cr–C(1) axis using B3LYP/DGDZVP. The perpendicular orientation conformer **5iii_a** is less favored by 0.10 kcal mol⁻¹ than conformer **5iii_e**. The difference is such small, the packing forces in the crystal lattice may overwhelm the preference, and the crystal structure **5iii_a** was observed.

B3LYP/DGDZVP calculations on compound **5** for rotational barrier (1.12 kcal mol⁻¹) of Cp ring with respect to Cp(cen.)–Cr axis was also made. The eclipsed conformer **5iii** (the minimum) is favored by 1.12 kcal mol⁻¹ over the staggered conformer **5iv** (the maximum).



The preference of transoid orientation of alkynyl ligand to a full π bond may explain that **5iii** is thermodynamically more stable than **5iv**. For comparison, the rotational barrier for compound **3** was also calculated (0.69 kcal mol⁻¹) using the same basis set. The smaller bond angle of Cp(cen.)–Cr–C(1) (114.90°) in compound **5** compared with Cp(cen.)–Cr–I (118.23°) in **3** (other bond angles: Cp(cen.)–Cr–N are compatible) and the perpendicular orientation of phenyl ring to Cp(Cr) ring might account for its greater rotational barrier than that for **3**. The values of rotational barrier obtained are greater than that for ferrocene (0.66 kcal mol⁻¹) [22] and less than the value calculated by McGlinchey in 1992 [23] for Cp-monosubstituted carbocation [(CO)₂(NO)Cr(C₅H₄–CH₂)]⁺ (7.3 kcal mol⁻¹). It is worth pointing out that for all three Cp-unsubstituted compounds, **3**, **5** and ferrocene, the theoretical treatment has given the eclipsed form more stable than the staggered one by 0.69, 1.12, and 0.66 kcal mol⁻¹, respectively. Whereas, a small barrier may be overwhelmed by various crystal structure factors making them deviated from the eclipsed configuration. The minimum energy occurring at $\omega = 0^\circ$, the theoretical calculation is consistent with the X-ray structure in the case of **5**. However, for compound **3**, possessing a smaller barrier (0.69 kcal mol⁻¹), a 18.8° rotation out of the eclipsed configuration of X-ray structure was observed (the minimum occurs at $\omega' = 53.2^\circ = (72 - 18.8^\circ)$). A gain in lattice energy might account for the preference. The same phenomenon was also observed in ferrocene [22], which also has a small barrier (0.66 kcal mol⁻¹). In ferrocene, the main contribution to the energy difference, favored the eclipsed form, is the induction energy of the metal in the potential field of the rings and the direct ring–ring electrostatic energy. Below the A -point transition at 164 K, the crystal of ferrocene is ordered and the structure is D_5 but with only a 9° rotation out of the D_{5h} eclipsed configuration.

3. Experimental details

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 Å) and P₂O₅. Hexane, pentane, benzene, and dichloromethane were dried over calcium hydride and freshly distilled under nitrogen. 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. Compounds **1** [2], **6** [1], and **12** [12] were prepared according to the literature procedures.

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

3.1. Preparation of (η^5 -cyclopentadienyl)dinitrosyl(phenylethynyl)chromium (**5**)

As this product is light sensitive, all operations were carried out with the exclusion of light. (η^5 -cyclopentadienyl)dinitrosylchlorochromium (**1**) (0.17 g, 0.81 mmol) was dissolved in 25 ml of diethylamine and phenylacetylene (0.11 ml, 0.98 mmol) was added while stirring. To this content cuprous iodide (0.018 g, 0.10 mmol) was added and the mixture was stirred for 6 h. The solvent was then removed under vacuum. The residue was extracted with 50 ml of diethyl ether. After the filtration and removal of the solvent under vacuum, the residue was dissolved in 30 ml of dichloromethane. Ten grams of silica gel were added and the solvent was then removed under vacuum. The residue was added to a dry-packed column (2.0 × 10 cm) of silica gel. Elution of the column with hexane/ether (3:1) gave two bands. The first band was unidentified. After removal of solvent, the second band gave (η^5 -cyclopentadienyl)dinitrosyl(phenylethynyl)chromium (**5**) (0.09 g, 42%). An X-ray sample, a dark brown crystal, was prepared by recrystallization using the solvent evaporation method from hexane: dichloromethane (8:3) at 0 °C for 48 h.

Anal. Calc. for C₁₃H₁₀O₂N₂Cr: C, 56.12; H, 3.62; N, 10.06. Found: C, 56.07; H, 3.26; N, 10.43%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 5.68 (5H, s, Cp); 7.18 (1H, t, $J = 8$ Hz, p -C₆H₅); 7.23 (2H, t, $J = 8$ Hz, m -C₆H₅); 7.40 (2H, d, $J = 8$ Hz, o -C₆H₅). Carbon-13 NMR (CDCl₃): δ (assignment): 100.20 (Cp); 114.18 (Ph–C=C); 122.70 (Ph–C=C); 125.94 (p -C₆H₅); 126.71 (i -C₆H₅); 127.94 (m -C₆H₅); 131.13 (o -C₆H₅). IR (KBr): ν (cm⁻¹) (intensity): 3098(w), 2359(w), 2104(w), 1805(vs), 1689(vs), 1484(w), 1424(w), 832(m). Mass spectrum: m/z 278(M⁺).

3.2. Preparation of (η^5 -carbomethoxycyclopentadienyl)dinitrosyl(phenylethynyl)chromium (**10**)

As this product is light sensitive, all operations were carried out with the exclusion of light. (η^5 -carbomethoxycyclopentadienyl)chlorodinitrosylchromium (**6**) (0.29 g, 0.81 mmol) was dissolved in 25 ml of diethylamine and phenylacetylene (0.13 ml, 1.12 mmol) was added while stirring. To this content cuprous iodide (0.02 g, 0.12 mmol) was added and the mixture was stirred for 16 h. The solvent was then removed under vacuum. The residue was extracted with 50 ml of diethyl ether. After the filtration and removal of the solvent under vacuum, the residue was dissolved in 30 ml of dichloromethane. Ten grams of silica gel were added and the solvent was then removed under vacuum. The residue was added to a dry-packed column (2.0 × 10 cm) of silica gel. Elution of the column with hexane/ether (1:1) gave two bands. The first band was unidentified. After removal of solvent, the second (dark brown) band (η^5 -carbomethoxycyclopentadienyl)dinitrosyl(phenylethynyl)chromium (**10**) (0.10 g, 38%) was obtained.

Anal. Calc. for C₁₅H₁₂O₄N₂Cr: C, 53.58; H, 3.60; N, 8.33. Found: C, 53.65; H, 3.83; N, 8.67%. Proton NMR(CDCl₃): δ (relative intensity, multiplicity, assignment): 3.72 (3H, s, –OCH₃); 5.43 (2H, t, $J = 2.4$ Hz, Cp H(3,4)); 6.05 (2H, t, $J = 2.4$ Hz, Cp H(2,5)); 7.27 (1H, t, $J = 8$ Hz, p -C₆H₅); 7.31 (2H, t, $J = 8$ Hz, m -C₆H₅); 7.40 (2H, d, $J = 8$ Hz, o -C₆H₅). Carbon-13 NMR (CDCl₃): δ (assignment): 53.01 (–OCH₃); 100.01 (Cp, C(3,4)); 102.37 (Cp, C(2,5)); 102.54 (Cr, C(1)); 127.11; 127.80; 128.27((Cr–C=C); i -C₆H₅); 127.23

(*p*-C₆H₅); 128.35(*m*-C₆H₅); 130.98 (*o*-C₆H₅); 160.68 (–COOCH₃). IR(KBr): ν (cm⁻¹) (intensity): 3079(s), 2361(s), 1825(vbs), 1724(vs), 1292(s), 1145(s), 862(s), 775(s). Mass spectrum: m/z 336(M⁺).

3.3. Preparation of (η^5 -carbomethoxycyclopentadienyl)tricarboonylchloro-tungsten (**12**)

(η^5 -Carbomethoxycyclopentadienyl)tricarboonylmethyltungsten (**11**) (0.45 g, 1.10 mmol) was dissolved in 15 ml of acetonitrile and chlorotrimethylsilane (0.29 ml, 2.20 mmol) was added. To this content was added sodium chloride (0.13 g, 2.2 mmol) and the mixture was refluxed for 5 h. The reaction mixture was poured into water, extracted with two portions of ether, and the combined extracts was dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 0.33 g (70%) of (η^5 -carbomethoxycyclopentadienyl)tricarboonylchlorotungsten (**12**) as red solid.

Anal. Calc. for C₁₀H₇WO₅Cl: C, 28.16; H, 1.65. Found: C, 27.91; H, 1.55%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 3.86 (–OCH₃); 5.88 (2H, t, J = 2.4 Hz, Cp H(3,4)); 6.13 (2H, t, J = 2.4 Hz, Cp H(2,5)). Carbon-13 NMR (CDCl₃): δ (assignment): 52.73 (–OCH₃); 94.95 (Cp, C(2,5)); 97.80 (Cp, C(3,4)); 95.61 (Cp, C(1)); 164.07 (–C(O)–); 212.88, 227.97 (W–CO). IR(KBr): ν (intensity): 2059(s), 2013(s), 1950(bvs), 1724(s), 1382(m), 1274(s), 1146(m), 835(m), 517(m) cm⁻¹. Mass spectrum: m/z 426(M⁺).

3.4. Preparation of (η^5 -carbomethoxycyclopentadienyl)tricarboonyl(phenylethynyl)tungsten (**13**)

As this product is light sensitive, all operations were carried out with the exclusion of light. (η^5 -Carbomethoxycyclopentadienyl)tricarboonylchlorotungsten (**12**) (0.35 g, 0.82 mmol) was dissolved in 25 ml of diethylamine and phenylacetylene (0.11 ml, 0.98 mmol) was added while stirring. To this content cuprous iodide (0.017 g, 0.09 mmol) was added and the mixture was stirred for 10 h. The solvent was then removed under vacuum. The residue was extracted with diethyl ether. After filtration and removal of the solvent under vacuum, the residue was dissolved in 30 ml of dichloromethane. Ten grams of silica gel were added and the solvent was then removed under vacuum. The residue was added to a dry-packed column (2.0 × 10 cm) of silica gel. Elution of the column with hexane/ether (3:1) gave two bands. The first band was unidentified. After removal of solvent, the second (yellow) band gave (η^5 -carbomethoxycyclopentadienyl)tricarboonyl(phenylethynyl)tungsten **13** (0.30 g, 74%).

Anal. Calc. for C₁₈H₁₂O₅W: C, 43.93; H, 2.46. Found: C, 43.69; H, 2.57%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 3.83 (–OCH₃); 5.73 (2H, t, J = 1.8 Hz, Cp H(3,4)); 6.09 (2H, t, J = 1.8 Hz, Cp H(2,5)); 7.14 (1H, t, J = 8 Hz, *p*-C₆H₅); 7.24 (2H, t, J = 8 Hz, *m*-C₆H₅); 7.29 (2H, d, J = 8 Hz, *o*-C₆H₅). Carbon-13 NMR (CDCl₃): δ (assignment): 52.58 (–OCH₃); 71.11 (W–C≡C) 91.91 (Cp, C(2,5)); 95.47 (Cp, C(3,4)); 95.99 (Cp, C(1)); 126.39 (*p*-C₆H₅); 126.68 (*i*-C₆H₅); 127.95 (*m*-C₆H₅); 129.87 (Ph–C≡C); 131.11 (*o*-C₆H₅); 164.10 (–C(O)–); 209.13, 226.52(W–C≡O). IR(KBr): ν (cm⁻¹) (intensity): 2965(w), 2359(w), 2030(w), 1981(vs), 1929(vs), 1727(s), 1629(m), 1453(m), 1282(m), 1146(m). Mass spectrum: m/z 492(M⁺).

3.5. X-ray diffraction analyses of **3**, **5** and **12**

The intensity data were collected on a CAD-4 diffractometer with a graphite monochromator (Mo K α radiation) for compound **5** and **12**; on Nicolet R3m/V diffractometer using ω scan for compound **3**. θ – 2θ scan data were collected at room temperature (24 °C). The data were corrected for absorption, Lorentz and polar-

ization effects. The absorption correction is according to the empirical psi rotation. The details of crystal data and intensity collection are summarized in Tables 8–10 for compound **3**, **5** and **12**, respectively.

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* [24]. All calculations were performed on a PC computer using SHELEX software package [25].

3.6. Computational method

Calculations based on DFT are carried out using B3LYP hybrid method involving three-parameter Becke exchange functional [26] and a Lee–Yang–Parr correlation functional [27]. All calculations are performed using the GAUSSIAN03 program [28]. The geometries for **3**, **5**, **6** and **12** are taken from the crystallographic data. For the B3LYP calculation [29,30], different basis sets are employed, DGDZVP for **3** and **5**, and LANL2DZ for **6** and **12**. The calculations are performed on HP RX5670 machine. The atomic charges have been analyzed using the natural population analysis (NPA) which yields reliable atomic charges and natural bond orbital

Table 8

Selected crystal data and refinement parameters for **3**

Empirical formula	C ₅ H ₅ N ₂ O ₂ ICr
Formula weight (g/mol)	304
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>Unit cell dimensions</i>	
a (Å)	6.892(3)
b (Å)	10.166(4)
c (Å)	12.682(7)
β (°)	100.91(4)
Volume (Å ³)	872.5(7)
Z	4
D_{calc} (Mg/m ³)	2.314
Absorption coefficient (mm ⁻¹)	4.737
$F(000)$	568
Crystal size (mm ³)	0.1 × 0.2 × 0.5
Diffractometer used	Nicolet R3m/V
Monochromator	Highly oriented graphite crystal
2θ range (°)	2.5–50.0
Scan type	$\theta/2\theta$
Scan speed °/min in ω	Variable; 2.93–4.65
Scan range, ω	1.00° plus K α -separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$0 \leq h \leq 9, 0 \leq k \leq 13, -16 \leq l \leq 16$
Reflections collected	1790 (1412 > 3 $\sigma(I)$)
Independent reflections	1549 (1350 > 3 $\sigma(I)$)
Extinction correction	$\chi = 0.0006(2)$, where $F^2 = F^2[1 + 0.002\chi^2/\sin(2\theta)] - 1/4$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w = 1/\sigma^2(F) + 0.0003F^2$
Final R indices (observed data) (%)	$R = 4.55, R_w = 5.36$
Goodness-of-fit	2.79
Largest and mean Δ/σ	0.001, 0.000
Data-to-parameter ratio	12.9:1
Largest difference in peak and hole (e Å ⁻³)	1.56 and –0.38

Table 9
Selected crystal data and refinement parameters for **5**

Empirical formula	C ₁₃ H ₁₀ CrN ₂ O ₂
Formula weight	278.23
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/m
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	6.4100(13)
<i>b</i> (Å)	8.9268(18)
<i>c</i> (Å)	11.161(2)
β (°)	91.28(3)
Volume (Å ³)	638.5(2)
<i>Z</i>	2
<i>D</i> _{calc} (Mg/m ³)	1.447
Absorption coefficient (mm ⁻¹)	0.890
<i>F</i> (000)	284
Crystal size (mm ³)	0.60 × 0.40 × 0.20
Theta range for data collection (°)	1.83–27.50
Index ranges	−8 ≤ <i>h</i> ≤ 8, −11 ≤ <i>k</i> ≤ 11, −14 ≤ <i>l</i> ≤ 14
Reflections collected	2828
Independent reflections [<i>R</i> _{int}]	1572 [0.0217]
Completeness to $\theta = 27.50^\circ$	100.0%
Absorption correction	ψ -scan
Maximum and minimum transmission	0.7377 and 0.5822
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1572/0/98
Goodness-of-fit on <i>F</i> ²	1.056
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0358, <i>wR</i> ₂ = 0.1061
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0459, <i>wR</i> ₂ = 0.1123
Extinction coefficient	0.013(5)
Largest difference in peak and hole (e Å ⁻³)	0.351 and −0.263

Table 10
Selected crystal data and refinement parameters for **12**

Empirical formula	C ₁₀ H ₇ ClO ₅ W
Formula weight	426.46
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	6.4464(2)
<i>b</i> (Å)	12.0258(4)
<i>c</i> (Å)	15.4957(6)
β (°)	90.926(1)
Volume (Å ³)	1201.12(7)
<i>Z</i>	4
<i>D</i> _{calc} (Mg/m ³)	2.358
Absorption coefficient (mm ⁻¹)	9.844
<i>F</i> (000)	792
Crystal size (mm ³)	0.40 × 0.05 × 0.03
θ range for data collection (°)	2.14–26.37
Index ranges	−7 ≤ <i>h</i> ≤ 8, −14 ≤ <i>k</i> ≤ 15, −19 ≤ <i>l</i> ≤ 19
Reflections collected	7725
Independent reflections [<i>R</i> _{int}]	2443 [0.0426]
Completeness to $\theta = 26.37^\circ$ (%)	99.7
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.7567 and 0.1105
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2443/0/156
Goodness-of-fit on <i>F</i> ²	1.094
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0304, <i>wR</i> ₂ = 0.0680
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0432, <i>wR</i> ₂ = 0.0713
Extinction coefficient	0.0026(3)
Largest difference in peak and hole (e Å ⁻³)	1.120 and −0.983

(NBO) calculations [31]. 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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