

Synthesis and characterization of tricarbonyl[η^6 -(phenylethynyl) arene]chromium complexes: crystal structure of tricarbonyl[η^6 -(3-phenylethynyl) anisole]chromium

Fung-E Hong^{*}, Shih-Chun Lo, Ming-Woei Liou, Yuan-Terng Chang, Chu-Chieh Lin

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan

Received 22 February 1995; in revised form 5 April 1995

Abstract

Tricarbonyl(η^6 -diphenylacetylene)chromium (**4**) was prepared from the reaction of tricarbonyl(η^6 -fluorobenzene)chromium (**3**) with lithium phenylacetylide (**2**) at a low temperature using hexamethylphosphoric triamide as cosolvent. A concomitant tricarbonyl(η^6 -butoxybenzene)chromium (**6**) was also obtained in this reaction probably owing to both the air oxidation of *n*-BuLi and the ring opening of tetrahydrofuran by *n*-BuLi. The overwhelming abundance of *meta* and *ortho* products **9b** and **10b** produced in the substitution reaction of tricarbonyl(η^6 -4-fluoroanisole)chromium (**8b**) by lithium phenylacetylide demonstrates that the reaction was by no means through the straightforward S_NAr mechanism. The results provide support for the mechanism proposed by Pauson and Brookhart, in which the nucleophile attacked a carbon of the phenyl ring not bearing the leaving group, followed by hydrogen migration and finally elimination of the leaving group to achieve aromaticity. In addition, compounds were characterized by mass, IR, 1H and ^{13}C NMR spectra, and elemental analysis. The molecular structure of tricarbonyl[η^6 -(3-phenylethynyl)anisole]chromium (**9b**) has been determined by X-ray diffraction studies. Crystal data are as follows: $P\bar{1}$; $a = 7.782(2)$ Å, $b = 8.910(2)$ Å and $c = 12.688(3)$ Å; $\alpha = 108.46(3)^\circ$, $\beta = 96.05(3)^\circ$ and $\gamma = 103.19(3)^\circ$; $V = 797.3(4)$ Å³; $Z = 2$; $R = 3.23\%$; $R_w = 4.37\%$.

Keywords: Chromium; Nucleophilic substitution; Phenylethynylarene

1. Introduction

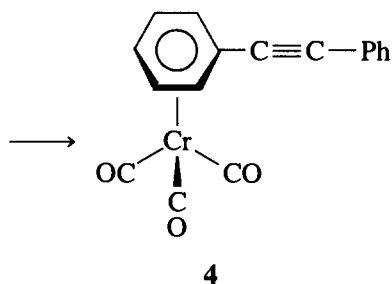
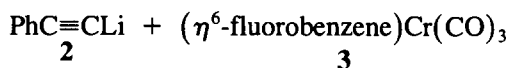
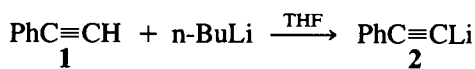
The complexation of $M(CO)_3$ ($M = Cr, Mo$ or W) to phenyl ring of various compounds has been extensively studied [1]. Generally, (η^6 -arene) $M(CO)_3$ complexes can be obtained by refluxing mixture of $M(CO)_6$ and the corresponding arene with or without adding another solvent [2,3]. However, attempts to coordinate the $M(CO)_3$ moiety to phenyl rings bearing alkyne moieties (e.g. diphenylacetylene) by direct reaction always resulted in extremely low yields [4]. It can be rationalized that $M(CO)_6$ reacts predominately with the triple bond instead of the phenyl rings of diphenylacetylene. Furthermore, extant efforts [5] for nucleophilic displacement of chloride from (η^6 - ClC_6H_5) $Cr(CO)_3$, employing more reactive carbanions such as $HC\equiv CLi$, $MeLi$ or $PhLi$ as nucleophiles were also all unsuccessful. The fact that the strong nucleophiles tend to attack the

phenyl ring at a position not bearing the leaving group and the poor leaving ability of chloride might be the chief reasons that these reactions fail. Recently, attempts to synthesize tricarbonyl[η^6 -phenylethynyl]arene]chromium were reported through palladium-catalyzed procedures [6]. Because this kind of compound is of fundamental interest in electronic features of metal-arene interactions [3] and the application [7] to synthesis using the alkyne function is quite practical, therefore our work has been motivated to develop another synthetic pathway to prepare tricarbonyl[η^6 -phenylethynyl]arene]chromiums.

2. Results and discussion

Tricarbonyl(η^6 -diphenylacetylene)chromium (**4**) was obtained from the reaction of tricarbonyl(η^6 -fluorobenzene)chromium (**3**) [2] with lithium phenylacetylide (**2**) in tetrahydrofuran (THF) at low temperature with a

^{*} Corresponding author.

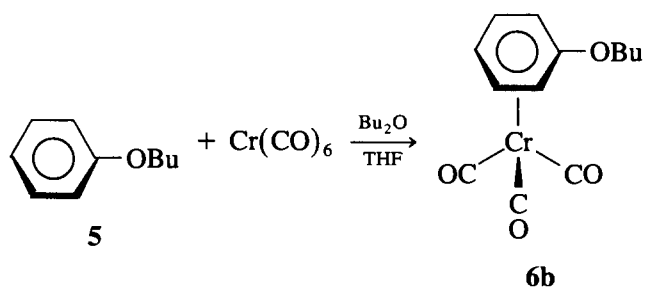


Scheme 1.

33% yield and could be promoted to a 44% yield by incorporating with hexamethylphosphoric triamide (HMPA) [8] (Scheme 1).

Reported evidence has elucidated that the reactivity of the (η^6 -haloarene) CrCO_3 complexes towards substitution is in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ [9]. Previous examples have also employed similar reactions to prepare a variety of compounds [3,10]. Therefore tricarbonyl(η^6 -fluorobenzene)chromium was selected as the electrophile. Lithium phenylacetylide was selected as the nucleophile. Hexamethylphosphoric triamide was introduced as cosolvent to increase the nucleophilicity of lithium phenylacetylide (2), if necessary. Accordingly, the reaction procedure was executed as follows: the $\text{PhC}\equiv\text{CLi}$ was first generated from $n\text{-BuLi}$ and $\text{PhC}\equiv\text{CH}$ in THF by mixing the reagents and then followed by adding HMPA and tricarbonyl(η^6 -fluorobenzene)chromium (3) at -78°C . The mixture was kept at -78°C for 1 h before being placed in a -50°C bath and then kept at that temperature for another 12 h. The reaction condition is critical to the products [11]. The augmentation of yield from 33% to 44% by adding HMPA demonstrates that the nucleophilicity of lithium phenylacetylide (2) is effectively enhanced by the polar aprotic solvent.

Interestingly, tricarbonyl(η^6 -butoxybenzene)chromium (6a) was also obtained with a 20% yield as the major side product under the above reaction condition.



Scheme 2.

In order to confirm the formation of 6a, we further independently carried out an alternative reaction of butyl phenyl ether with $\text{Cr}(\text{CO})_6$ by refluxing Bu_2O -THF solution to give rise to a 93% yield of 6b, as shown in Scheme 2. The identity of the compound was confirmed by exhibiting identical patterns obtained by ^1H and ^{13}C NMR spectroscopy, mass spectroscopy (MS) and IR spectroscopy. The unexpected side product 6 might result from the attack of 3 by $n\text{-BuOLi}$, owing to either air oxidation of $n\text{-BuLi}$ [12] or ring opening of THF by $n\text{-BuLi}$. Ring opening of THF was observed in the presence of alkyl lithium or Lewis acids [13]. Recently, the ring opening of THF with a subsequent reaction on an osmium cluster was reported by Shore and coworkers [14]. As a good nucleophile, $n\text{-BuOLi}$ readily proceeded via a substitution reaction with tricarbonyl(η^6 -fluorobenzene)chromium (3), competing with $\text{PhC}\equiv\text{CLi}$ under the reaction condition described above. Hence, when this reaction was carried out with fresh $n\text{-BuLi}$ and at a low temperature, the production of 6 could be reduced to a minimum amount.

The R_f values of 4, 6 and unreacted 3 in thin layer chromatography are very similar. A slightly difference of solubility in hexane makes the separation of these compounds by centrifugal thin layer chromatography (CTLC) possible. Compound 4 is orange; 3 is yellow. A deeper color of the former than the latter compound might be due to the conjugated multiple bonds of the former compound.

Several 3-related compounds, namely 8a, 8b and 8c, were prepared utilizing literature methods [2,15]. The nucleophilic displacement of fluoride from tricarbonyl(η^6 -4-fluoroanisole)chromium (8b) was carried out un-

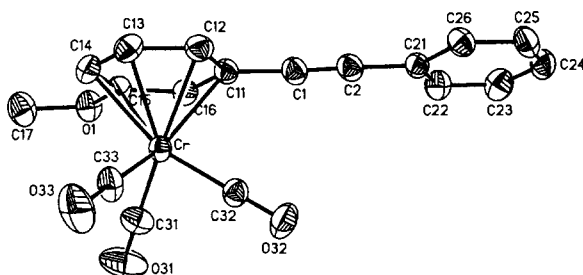
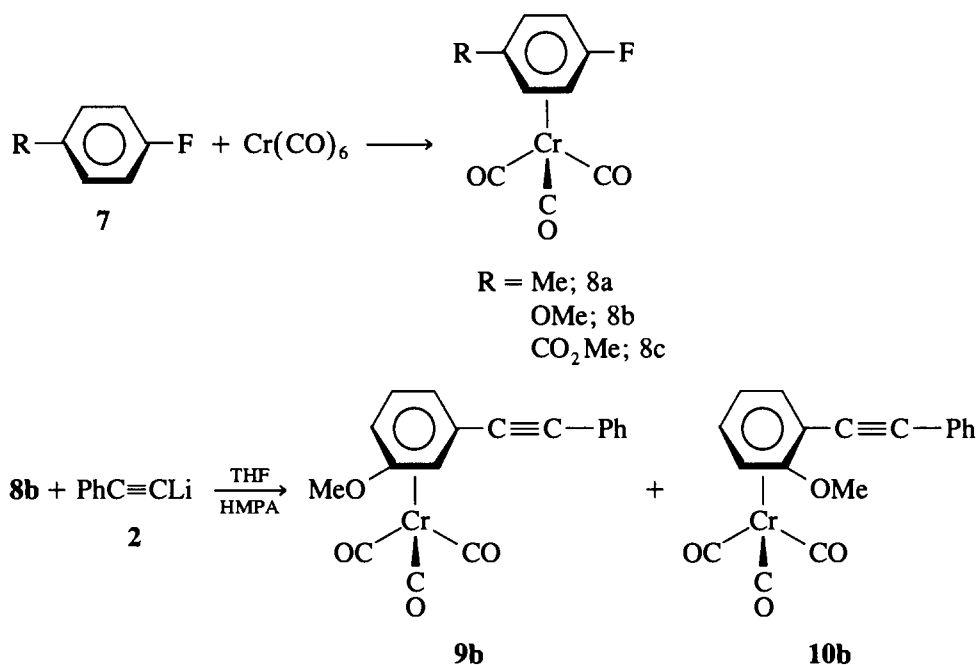


Fig. 1. ORTEP drawing with the numbering scheme of 9b. Hydrogen atoms were omitted for clarity.

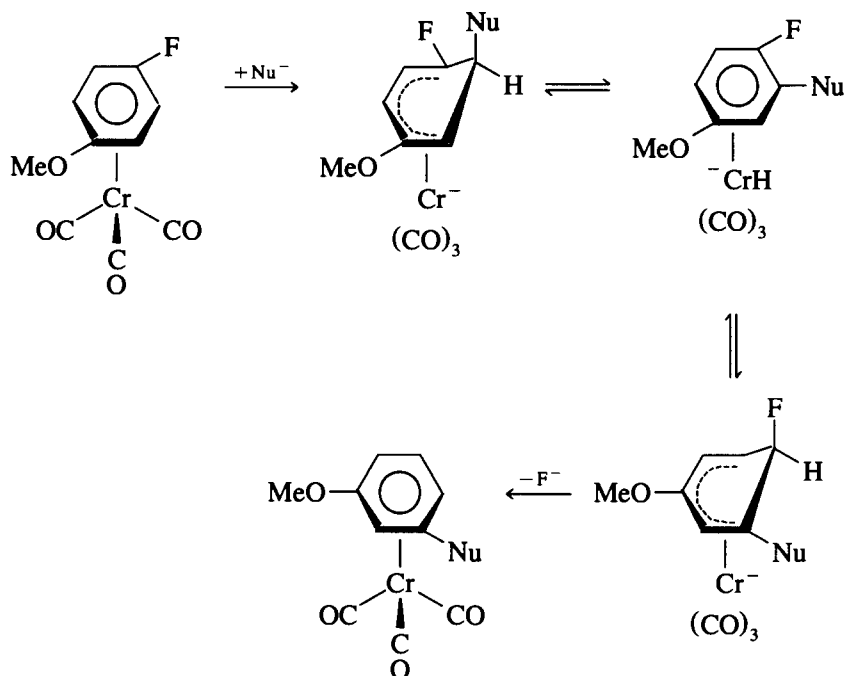


Scheme 3.

der the same reaction conditions, including taking advantage of HMPA [16], as described above. Strikingly, the expected *para* product was not isolated in the reaction conditions. However, two unexpected products, *ortho* and *meta*, were obtained. The ratio of **9b** to **10b** was about 2 to 1, integrated from the crude ^1H NMR spectrum, with an overall isolated yield of 41%.

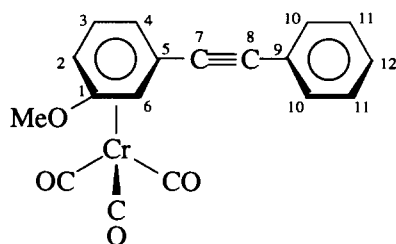
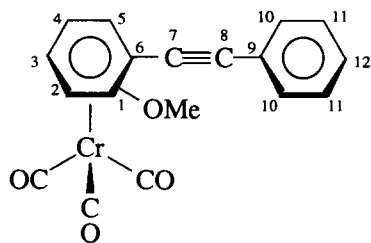
In the ^1H NMR spectrum, product **9b** exhibits one distinctive singlet at 5.32 ppm belonging to the 1H of

$\text{C}_6\text{-H}$, one triplet, collapsed by a doublet of doublets, at 5.57 ppm due to the 1H of $\text{C}_3\text{-H}$ as well as two doublets overlapping at 5.09 ppm for the 2H of $\text{C}_2\text{-H}$ & $\text{C}_4\text{-H}$. On the contrary, **10b** shows two sets of significant triplets, collapsed by a doublet of doublets, at 5.54 ppm and 4.93 ppm, corresponding to $\text{C}_3\text{-H}$ and $\text{C}_4\text{-H}$, respectively. Furthermore, there are two sets of doublets at 5.86 ppm and 5.13 ppm corresponding to $\text{C}_5\text{-H}$ and $\text{C}_2\text{-H}$ respectively [17]. Single crystal X-ray



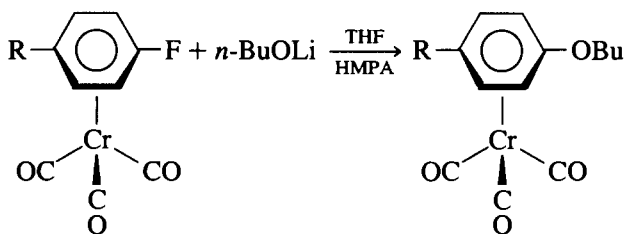
Scheme 4.

determination of **9b** revealed that this compound is indeed as we expected and is shown in Fig. 1.

**9b****10b**

The fact that *ortho* and *meta* products were obtained instead of the *para* product was noteworthy. Such result distinctly differs from the observation by Brown and Raju [3]. They reported that exclusively *para*-substituent product was obtained when tricarbonyl(η^6 -4-fluorotoluene)chromium (**8a**) reacted with methoxide ion in methanol, and thereby they ruled out this substitution reaction via a benzyne intermediate which would lead to predominately the *meta* derivative. Therefore the mechanism of obtaining overwhelming *meta*- and *ortho*-dominate products, shown in Scheme 3, was more complicated and different from the straightforward nucleophilic aromatic substitution. An alternative mechanism [9], proposed by Pauson and Brookhart, involving hydrogen migration via the metal would be consistent with our results, as depicted in Scheme 4. In that mechanism, the nucleophilic attack took place on a carbon atom of the phenyl ring not bearing the leaving group, followed by hydrogen migration and finally elimination of the leaving group to achieve aromaticity.

Nevertheless, similar results were not obtained for **8a** and **8c** as in the case of **8b**. Instead, tricarbonyl(η^6 -4-

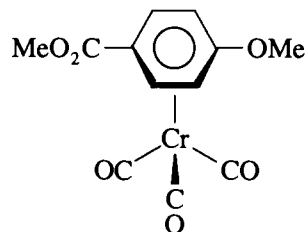


R = Me; **8a**
OMe; **8b**
CO₂Me; **8c**

R = Me; **11a**
OMe; **11b**
CO₂Me; **11c**

Scheme 5.

butoxytoluene)chromium (**11a**) was obtained with a 44% yield when compound **8a** was reacted with lithium phenylacetylide (**2**) at a higher temperature [18]. In this case, the butoxyl group is a better nucleophile than phenylacetylide. The former attacked **8a** much more rapidly than the latter and resulted in predominate **11a**, **12** and **11c** were obtained with 15% and 5% yields respectively when **8c** was reacted with lithium phenylacetylide under the normal reaction conditions.

**12**

Compound **12** might arise from the direct attack of the carbon which bears the fluoride of tricarbonyl(η^6 -4-fluoromethylbenzoate)chromium (**8c**) by the methoxide ion released from methyl ester by the attack of lithium phenylacetylide. This result also indicated that the substitution reaction of ester is easier than displacement of fluoride by lithium phenylacetylide (**2**). In the case of **11a** and **11c**, the formation of the exclusive *para*-derivative products were consistent with the result in [3], as shown in Scheme 5. Again, butoxyl group attacked **8a** and **8c** much more rapidly than phenylacetylide.

3. Experimental section

3.1. Apparatus and materials

All operation were performed in a nitrogen-flushed glove-box or in a vacuum system. Freshly distilled solvents were used. All processes of separation of the products were performed by TLC (Chromatotron, Harrison model 8924). ¹H and ¹³C NMR spectra were recorded (Varian-300 spectrometer) at 300 MHz and 75.46 MHz respectively; chemical shifts are reported in ppm relative to internal tetramethylsilane. IR spectra of solution in CH₂Cl₂ were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on a JEOL JMS-SX/SX 102A GC/MS/MS. Elementary analyses were recorded on a Heraeus CHN-O-S-RAPID analyzer.

3.2. General procedure for preparations of **4**, **9b** and **10b**

Into a spherical flask (100 ml) equipped with a condenser and a magnetic stirrer were placed 0.5 ml of

PhC≡CH (4.55 mmol) and 20 ml of THF. The solution was placed in -78°C bath and stirred for several minutes. 1.55 ml of *n*-BuLi (2.5 M) was added and stirred for 1 h at -78°C . ($\eta^6\text{-C}_6\text{H}_6\text{F}$)Cr(CO)₃ (900 mg, 3.88 mmol), dissolved in 20 ml of THF, was transferred to the reaction flask. The solution was stirred at -50°C for 12 h before raising the temperature to room temperature. It was stirred for another 12 h at room temperature. After the reaction was completed, the solution was exposed to air for several hours. The mixture was filtered by silica gel, and the solvent removed in vacuum.

The residue was dissolved in a small amount of CH₂Cl₂ and then was subjected to CTLC for separation. The *R_f* values of **4**, **6** and unreacted **3** are very similar. A slightly difference of solubility in hexane makes the separation of these compounds by CTLC possible. Three bands were collected through the elute of hexane. The first yellow band was identified as small amount of unreacted ($\eta^6\text{-C}_6\text{H}_6\text{F}$)Cr(CO)₃. Compound **4** (orange) was collected as the second band. The third band was yellow containing **6**. The separation in CTLC was done under nitrogen.

4: Yield, 0.40 g, 1.28 mmol (33%). ¹H NMR (CDCl₃): δ 5.28 (m, 1H, *p*-arene), 5.38 (m, 2H, *o*-arene), 5.55 (m, 2H, *m*-arene), 7.37 (m, 3H, *m* and *p*-C₆H₅), 7.52 (m, 2H, *o*-C₆H₅) ppm. ¹³C NMR (CDCl₃): δ 77.115 (1C, -C≡C-), 77.204 (1C, -C≡C-), 90.503 (1C, *p*-arene), 91.589 (2C, *o*-arene), 94.749 (2C, *m*-arene), 117.20 (1C, *ipso*-arene), 128.475 (2C, *m*-C₆H₅), 129.143 (1C, *p*-C₆H₅), 132.000 (2C, *o*-C₆H₅), 138.200 (1C, *ipso*-C₆H₅), 232.271 (3C, 3CO) ppm. IR(CH₂Cl₂): $\nu(\text{CO})$ 1900, 1976 cm⁻¹. MS: *m/z* 314 (P⁺). Anal. Found: C, 64.71; H, 3.22. Calc.: C, 64.97; H, 3.21%.

6: Yield, 0.23 g, 0.79 mmol (20%). ¹H NMR (CDCl₃): δ 0.96 (t, *J* = 7.2 Hz, 3H, -CH₃), 1.47 (m, 2H, -OBu), 1.73 (m, 2H, -OBu), 3.84 (d, *J* = 6.4 Hz, 2H, -OCH₂), 4.86 (m, 1H, *p*-arene), 5.10 (d, *J* = 6.6 Hz, 2H, *o*-arene), 5.54 (m, 2H, *m*-arene) ppm. ¹³C NMR (CDCl₃): δ 13.737 (1C, -Bu), 19.067 (1C, -Bu), 30.866 (1C, -Bu), 68.493 (1C, -Bu), 78.436 (2C, *m*-C₆H₅), 85.147 (1C, *p*-C₆H₅), 95.120 (2C, *o*-C₆H₅), 142.953 (1C, *ipso*-C₆H₅), 233.248 (3C, 3CO) ppm. IR(CH₂Cl₂): $\nu(\text{CO})$ 1880, 1968 cm⁻¹. MS: *m/z* 286 (P⁺). Anal. Found: C, 54.70; H, 4.99. Calc. C, 54.55; H, 4.93%.

9b: ¹H NMR (CDCl₃): δ 3.76 (s, 3H, OMe), 5.09 (unresolved dd, 2H, C₂-H and C₄-H), 5.32 (s, 1H, C₆-H), 5.57 (dd, *J*₃₂ = 6.4 Hz, *J*₃₄ = 6.4 Hz, 1H, C₃-H), 7.38 (m, 3H, 2C₁₁-H and C₁₂-H), 7.54 (m, 2H, 2C₁₀-H) ppm. ¹³C NMR (CDCl₃): δ 55.690 (3C, OMe), 77.196 (1C, C₃), 79.937 (1C, C₄), 85.242 (1C, C₈), 88.055 (1C, C₆), 90.512 (1C, C₇), 92.603 (1C, C₅), 93.618 (1C, C₂), 121.675 (1C, C₁), 128.484 (1C, C₁₁), 129.267 (1C, C₁₂), 132.044 (1C, C₁₀), 142.299

(1C, C₉), 232.948 (3C, 3CO) ppm. IR(CDCl₃): $\nu(\text{CO})$ 1902, 1976 cm⁻¹. MS: *m/z* 344 (P⁺).

10b: ¹H NMR (CDCl₃): δ 3.86 (s, 3H, OMe), 4.93 (dd, *J*₄₃ = 6.4 Hz, *J*₄₅ = 6.4 Hz, 1H, C₄-H), 5.13 (d, *J*₂₃ = 6.5 Hz, 1H, C₂-H), 5.54 (ddd, *J*₃₅ = 1.1 Hz, *J*₃₄ = 6.4 Hz, *J*₃₂ = 6.5 Hz, 1H, C₃-H), 5.86 (dd, *J*₅₃ = 1.1 Hz, *J*₅₄ = 6.4 Hz, 1H, C₅-H), 7.36 (m, 3H, 2C₁₁-H and C₁₂-H), 7.54 (C₁₀-H) ppm. ¹³C NMR (CDCl₃): δ 56.242 (3C, OMe), 73.484 (1C, C₄), 80.008 (1C, C₇), 82.136 (1C, C₈), 84.601 (1C, C₃), 92.283 (1C, C₆), 92.639 (1C, C₅), 98.167 (1C, C₂), 122.378 (1C, C₁), 128.350 (1C, C₁₁), 128.822 (1C, C₁₂), 131.964 (1C, C₁₀), 142.841 (1C, C₉), 232.485 (3C, 3CO) ppm. IR(CDCl₃): $\nu(\text{CO})$ 1904, 1976 cm⁻¹. MS: *m/z* 344 (P⁺).

11a: ¹H NMR (CDCl₃): δ 0.96 (t, *J* = 7.3 Hz, 3H, -CH₃), 1.45 (m, 2H, -OBu), 1.71 (m, 2H, -OBu), 2.07 (s, 3H, -CH₃), 3.79 (t, *J* = 6.3 Hz, 2H, -OCH₂), 5.13 (d, *J* = 6.9 Hz, 2H, *o*-arene), 5.42 (d, *J* = 6.9 Hz, 2H, *m*-arene) ppm. ¹³C NMR (CDCl₃): δ 13.668 (1C, -Bu), 19.000 (1C, -Bu), 19.774 (1C, -CH₃), 30.838 (1C, -Bu), 68.650 (1C, -Bu), 79.234 (2C, *m*-arene), 95.756 (2C, *o*-arene), 101.549 (1C, *ipso*-arene), 141.061 (1C, *ipso*-arene), 233.882 (3C, 3CO) ppm. IR(CDCl₃): $\nu(\text{CO})$ 1890, 1970 cm⁻¹. MS: *m/z* 300 (P⁺).

11b: ¹H NMR (CDCl₃): δ 0.95 (t, *J* = 7.2 Hz, 3H, -CH₃), 1.43 (m, 2H, -OBu), 1.68 (m, 2H, -OBu), 3.64

Table 1
Crystal data of **9b**

Formula weight	C ₁₈ H ₁₂ CrO ₄
Formula weight	344.3
Crystal system	Triclinic
Space group	P $\bar{1}$
<i>a</i> (Å)	7.782(2)
<i>b</i> (Å)	8.910(2)
<i>c</i> (Å)	12.688(3)
α (°)	108.46(3)
β (°)	96.05(3)
γ (°)	103.19(3)
<i>V</i> (Å ³)	797.3(4)
<i>Z</i>	2
<i>D_c</i> (g cm ⁻³)	1.434
λ (Mo K α) (Å)	0.71073
μ (mm ⁻¹)	0.734
Range (°)	4.0 to 50.0
Scan type	θ -2 θ
Number of reflections collected	3052
Number of independent reflections	2825 (<i>R</i> _{int} = 0.96%)
Number of observed reflections	2378 (<i>F</i> > 4.0 σ (<i>F</i>))
Number of refined parameters	208
<i>R_f</i> ^a for significant reflections	0.0323
<i>R_w</i> ^b for significant reflections	0.0437
Goodness of fit ^c	1.31

$$^a R_f = \sum(F_o - F_c) / \sum F_o$$

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

$$^c \text{Goodness of fit} = [\sum w(F_o - F_c)^2 / (N_{\text{rftns}} - N_{\text{params}})]^{1/2}. W^{-1} = \sigma^2(F) + 0.0010F^2.$$

Table 2
Atomic coordinates and equivalent isotropic displacement coefficients for **9b**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq}^a ($\times 10^{-3} \text{ \AA}^2$)
Cr	2274(1)	1029(1)	2095(1)	40(1)
C(31)	2125(4)	117(3)	3203(2)	63(1)
O(31)	2027(4)	-456(3)	3891(2)	111(1)
C(32)	-181(3)	486(3)	1739(2)	50(1)
O(32)	-1730(3)	122(3)	1488(2)	76(1)
C(33)	2151(4)	-1012(3)	1097(2)	59(1)
O(33)	2055(4)	-2294(3)	464(2)	102(1)
O(1)	5835(2)	3087(2)	4182(2)	62(1)
C(1)	928(4)	4428(3)	2422(2)	56(1)
C(11)	2349(3)	3632(3)	2323(2)	48(1)
C(12)	2702(3)	2851(3)	1236(2)	53(1)
C(13)	4086(3)	2099(3)	1156(2)	56(1)
C(14)	5178(3)	2131(3)	2122(2)	54(1)
C(15)	4861(3)	2934(3)	3187(2)	49(1)
C(16)	3399(3)	3629(3)	3285(2)	48(1)
C(17)	7250(4)	2284(4)	4144(3)	79(2)
C(2)	-205(4)	5132(3)	2479(2)	57(1)
C(21)	-1641(3)	5920(3)	2515(2)	50(1)
C(22)	-2107(4)	6707(4)	3526(2)	64(1)
C(23)	-3536(4)	7385(4)	3526(3)	73(1)
C(24)	-4481(4)	7304(3)	2534(3)	68(1)
C(25)	-4015(4)	6554(4)	1526(3)	66(1)
C(26)	-2598(4)	5862(3)	1508(2)	59(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(s, 3H, OMe), 3.75 (t, $J = 6.0$ Hz, 2H, $-\text{OCH}_2$), 5.26 (s, 4H, arene) ppm. ¹³C NMR (CDCl_3): δ 13.641 (1C, $-\text{Bu}$), 18.982 (1C, $-\text{Bu}$), 30.865 (1C, $-\text{Bu}$), 56.385 (1C, OMe), 69.309 (1C, $-\text{Bu}$), 79.875 (4C, arene), 136.566 (2C, *ipso*-arene), 234.025 (3C, 3CO) ppm. IR(CDCl_3): $\nu(\text{CO})$ 1892, 1970 cm^{-1} . MS: m/z 316 (P^+).

11c: ¹H NMR (CDCl_3): δ 0.97 (t, $J = 6.8$ Hz, 3H, $-\text{CH}_3$), 1.43 (m, 2H, $-\text{OBu}$), 1.68 (m, 2H, $-\text{OBu}$), 3.76 (s, 3H, OMe), 4.27 (t, $J = 6.6$ Hz, 2H, $-\text{OCH}_2$), 5.13 (m, 2H, *o*-arene), 6.27 (m, 2H, *m*-arene) ppm. ¹³C NMR (CDCl_3): δ 13.500 (1C, $-\text{Bu}$), 18.927 (1C, $-\text{Bu}$), 30.478 (1C, $-\text{Bu}$), 55.749 (1C, OMe), 65.326 (1C, $-\text{Bu}$), 76.746 (2C, arene), 95.402 (2C, arene), 144.213

Table 3
Selected bond distances (\AA) and angles ($^\circ$)

Bond distances			
Cr–C(31)	1.834(3)	Cr–C(32)	1.829(3)
Cr–C(33)	1.832(3)	Cr–C(11)	2.230(3)
Cr–C(12)	2.211(3)	Cr–C(13)	2.186(3)
Cr–C(14)	2.242(3)	Cr–C(15)	2.284(2)
Cr–C(16)	2.234(2)	C(31)–O(31)	1.143(5)
C(32)–O(32)	1.155(3)	C(33)–O(33)	1.150(3)
O(1)–C(15)	1.352(3)	O(1)–C(17)	1.441(4)
C(1)–C(11)	1.439(4)	C(1)–C(2)	1.189(4)
C(11)–C(12)	1.422(4)	C(11)–C(16)	1.397(4)
C(12)–C(13)	1.389(4)	C(13)–C(14)	1.404(4)
C(14)–C(15)	1.393(4)	C(15)–C(16)	1.413(4)
C(2)–C(21)	1.446(4)	C(21)–C(22)	1.383(4)
C(21)–C(26)	1.389(4)	C(22)–C(23)	1.382(5)
C(23)–C(24)	1.360(5)	C(24)–C(25)	1.372(5)
C(25)–C(26)	1.379(5)		
Bond angles			
C(31)–Cr–C(32)	90.2(1)	C(31)–Cr–C(33)	87.9(1)
C(32)–Cr–C(33)	88.0(1)	Cr–C(31)–O(31)	179.8(2)
Cr–C(32)–O(32)	178.4(2)	Cr–C(33)–O(33)	179.2(3)
C(15)–O(1)–C(17)	117.9(2)	C(11)–C(1)–C(2)	176.9(3)
O(1)–C(15)–C(14)	125.1(3)	O(1)–C(15)–C(16)	114.9(2)
C(1)–C(2)–C(21)	177.4(2)		

(1C, *ipso*-arene), 144.438 (1C, *ipso*-arene), 231.132 (3C, 3CO) ppm. IR(CDCl₃): $\nu(\text{CO})$ 1716, 1914, 1986 cm⁻¹. MS:*m/z* 344 (P⁺).

12: ¹H NMR (CDCl₃): δ 3.77 (s, 3H, OMe), 3.86 (s, 3H, OMe), 5.14 (m, 2H, *o*-arene), 6.27 (m, 2H, *m*-arene) ppm. ¹³C NMR (CDCl₃): δ 52.744 (1C, OMe), 55.797 (1C, OMe), 79.314 (2C, *arene*), 95.292 (2C, *arene*), 144.310 (1C, *ipso*-arene), 148.764 (1C, *ipso*-arene), 165.468 (1C, CO), 230.794 (3C, 3CO) ppm. IR(CDCl₃): $\nu(\text{CO})$ 1722, 1912, 1988 cm⁻¹. MS:*m/z* 302 (P⁺).

3.3. Crystal structure determination of 9b

A red parallelepiped crystal of **9b** with a size of 0.2 × 0.4 × 0.5 mm was used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å. The positions of the heavy atoms in the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were considered to ride on carbon atoms with a C–H bond length of 0.96 Å, and the temperature factors were fixed at 0.08 Å². The hydrogen atoms were included for structure factor calculation in the final cycles. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVAX 3100 computer.

The crystallographic data of **9b** are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement coefficients are given in Table 2 and the bond lengths and angles in Table 3.

Acknowledgment

We thank the National Research Council of Taiwan (Grant NSC-84-2113-M-005-008) for support.

References and notes

[1] (a) J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987; (b) R. Davis and L.A.P. Kane-Maguire, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chem-*

istry, Vol. 3, Pergamon, Oxford, 1982, p. 953, and references cited therein; (c) W.E. Watts, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982, p. 1013; (d) R.P.A. Sneed, *Organochromium Compounds*, Academic Press, New York, 1975.

[2] C.A.L. Mahaffy and P.L. Pauson, *Inorg. Synth.*, 19 (1979) 154.

[3] D.A. Brown and J.R. Raju, *J. Chem. Soc. A*, (1966) 40.

[4] The yield of **4** is less than 1% from the direct reaction of Cr(CO)₆ with diphenylacetylene. (a) R.G. Knox, D.G. Leppard, P.L. Pauson and W.E. Watts, *J. Organomet. Chem.*, 34 (1972) 347; (b) A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, *J. Organomet. Chem.*, 102 (1975) 185.

[5] W.E. Watts in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982, p. 1027, and references cited therein.

[6] (a) D. Villemin and E. Schigeko, *J. Organomet. Chem.*, 293 (1985) C10; (b) M.E. Wright, *J. Organomet. Chem.*, 376 (1989) 353; (c) M.E. Wright, *Organometallics*, 8 (1989) 407.

[7] (a) J.J. Eisch, *Organometallic Syntheses*, Vol. 2, Academic Press, New York, 1981, p. 99, and references cited therein; (b) F.-E. Hong, Y.-T. Chang, M.-C. Cheng and Y. Wang, *Polyhedron*, 12 (1993) 1919; (c) F.-E. Hong, S.-C. Lo, M.-Y. Keng and Y.-T. Chang, *J. Chin. Chem. Soc.*, 41 (1994) 511.

[8] D. Seebach, *Angew. Chem., Int. Edn. Engl.*, 27 (1988) 1624.

[9] S.G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Vol. 2, Pergamon, Oxford, 1982, p. 170, and references cited therein.

[10] (a) J.F. Bunnett and H. Hermann, *J. Org. Chem.*, 36 (1971) 4081; (b) P.L. Pauson and C.A.L. Mahaffy, *J. Chem. Res. S*, (1979) 128; (c) M.J. McGlinchey and J.-S. Tan, *J. Am. Chem. Soc.*, 98 (1976) 2271; (d) R. Davis and L.A.P. Kane-Maguire, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*; Vol. 3, Pergamon, Oxford, 1982, p. 1043, and references cited therein.

[11] (a) M.F. Semmelhack and H.T. Hall, *J. Am. Chem. Soc.*, 96 (1974) 7091; (b) J.A. Heppert, M.A. Morgenstern, D.M. Scherubel, F. Takusagawa and M.R. Shaker, *Organometallics*, 7 (1988) 1715; (c) J.A. Heppert, M.E. Thomas-Miller, D.M. Scherubel, F. Takusagawa, M.A. Morgenstern and M.R. Shaker, *Organometallics*, 8 (1989) 1199; (d) T.J. Henly, C.B. Knobler and M.F. Hawthorne, *Organometallics*, 11 (1992) 2313.

[12] J.J. Eisch, *Organometallic Syntheses*, Vol. 2, Academic Press, New York, 1981, p. 90.

[13] (a) B. Nicholls, M.C. Whiting, *J. Chem. Soc.*, (1959) 551; (b) W. Strohmeier, *Chem. Ber.*, 94 (1961) 2490.

[14] (a) D.P. Workman and S.G. Shore, in G.A. Olah, K. Wade and R. Williams (eds.), *Electronic Deficient Boron and Carbon Clusters*, Wiley, New York, 1991, Chapter 10; (b) D.-Y. Jan, D.P. Workman, L.-Y. Hsu, J.A. Krause and S.G. Shore, *Inorg. Chem.*, 31 (1992) 5123.

[15] The reaction was performed by the procedure described in [3] except with a prolonged reaction time to 3.5 days. TLC was used as the purification method.

[16] No desired product could be obtained without adding HMPA in this reaction.

[17] There is a long-range coupling between C₃-H and C₅-H with $J_{35} = 1.1$ Hz.

[18] In addition, about 17% of starting material was recovered.