**Pergamon**

PII: S0277–5387(96)00518–9

# Nucleophilic substitution reactions of cyclopentadienyl and its related carbanions on tricarbonyl($\eta^6$-4-fluorotoluene)chromium: molecular structures of 1,4-bis [tricarbonyl($\eta^6$-4-toluene)chromium] cyclopentadiene, 3-[tricarbonyl($\eta^6$-4-toluene)chromium]indene, and 9,9-bis[tricarbonyl($\eta^6$-4-toluene) chromium]fluorene

Fung-E Hong,* Yaw-Cherng Yang, Shih-Chun Lo and Chu-Chieh Lin

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan, R.O.C.

**Abstract**—3-[Tricarbonyl($\eta^6$-4-toluene)chromium]indene (**4**) was obtained as the only separated product from the nucleophilic substitution of tricarbonyl($\eta^6$-4-fluorotoluene)chromium (**1**) with indenyl lithium. Presumably, a 1,3-shift of benzylic proton takes place after the attack of (**1**) by indenyl lithium during the formation of (**4**). Under similar reaction conditions, 1,4-bis[tricarbonyl($\eta^6$-4-toluene)chromium]cyclopentadiene (**3**) was detected as the only separated bimetallic product from continuous nucleophilic substitutions of cyclo-pentadienyl by (**1**). In this case, a 1,2-shift of the benzylic proton was observed during the formation of (**3**). Also, 9,9-bis[tricarbonyl($\eta^6$-4-toluene)chromium]fluorene (**7**) was obtained from the consecutive nucleophilic substitutions of fluorenyl by (**1**). No proton shift is possible after the formation of (**7**). Presumably, the nucleophilic substitutions take place directly on the fluorine-bearing carbon in all these cases. Compounds were characterized by mass, infrared, $^1$H, $^{13}$C NMR spectra. The molecular structures of **3**, **4**, and **7** have been determined by X-ray diffraction. © 1997 Elsevier Science Ltd. All rights reserved.

*Keywords*: nucleophilic substitution; chromium; bridging π-ring ligand; proton shift; cyclopentadienyl; bimetallic compound

The chemistry of nucleophilic substitutions on (arene) Cr(CO)$_3$ and its related compounds has been intensively investigated because of both fundamental interest in structural and electronic features of metal–arene interactions and various applications in organic synthesis [1]. Recently, chemical reactions involving two or more (arene)Cr(CO)$_3$ moieties combined by bridging π-ring have attracted interest [2]. However, examples of the synthesis of multiple metal com-

pounds through bridging π-rings are few [3]. We now report the preparations and characterizations of some chromium-containing bimetallic compounds.

The thermal, suprafacial *vs* antarafacial, sig-matropic 1,5 and 1,3 shifts of alkyl groups in geminally substituted cyclopentadienes has been known to take place at elevated temperatures [4]. Here, we report some examples of 1,2- or 1,3-shifts of protons during the nucleophilic substitution of tricarbonyl ($\eta^6$-4-fluorotoluene)chromium (**1**) by cyclopentadienyl and its related compounds under much lower temperature.

---

*Author to whom correspondence should be addressed.

## RESULTS AND DISCUSSION

The nucleophilic substitution of tricarbonyl($\eta^6$-4-fluorotoluene)chromium (1) by cyclopentadienyl was carried out in tetrahydrofuran first at $-78°C$ and then the reaction temperature was raised gradually to 25°C (Scheme 1). 1-Tricarbonyl[($\eta^6$-4-toluene)chromium] cyclopentadiene (2) was yielded instead of 5-tricarbonyl[($\eta^6$-4-toluene)chromium]cyclopentadiene (2'), which might be formed by the direct substitution of the fluoride atom by the cyclopentadienyl anion. It was confirmed by the observation of a $CH_2$ signal in the $^1H$ NMR of the product as well as the existence of a 2° carbon by $^{13}C$ DEPT NMR. (2) was further characterized by $^1H$ NMR, $^{13}C$ NMR, IR, and mass spectra. It is obvious that a 1,2-hydrogen shift took place after the attack of cyclopentadienyl on the fluoride-bearing carbon in (1) during the formation of (2). The fact that the hydrogen shift took place under such a low temperature is noteworthy. Further reaction of (1) with deprotonated (2) again was carried out as well. 1,4-Bis[tricarbonyl($\eta^6$-4-toluene) chromium]cyclopentadiene (3) was obtained as the only separated bimetallic product. (3) was characterized by mass, infrared, $^1H$, $^{13}C$ NMR spectra as well as X-ray crystal structural determination. It shows that two $Cr(CO)_3$ fragments are in opposed directions (Fig. 1). This could result from the packing effect in the solid state. The two (arene)$Cr(CO)_3$ fragments might actually rotate freely in solution. The dihedral angles of two arene and cyclopentadiene rings are 6.1 and 7.5°, respectively. They are almost coplanar thus to obtain the best delocalization of $\pi$ electrons. The bond lengths of C(1)—C(5) and C(3)—C(4) are 1.355 and 1.344 Å, respectively. Accordingly, they are typical double bonds (Table 2).

The five carbon atoms of the Cp ring, C(1), C(2), C(3), C(4) and C(5), are almost coplanar. C(2) is only slightly, (0.0178 Å), off the plane of cyclopentadiene. Again, a 1,2 hydrogen shift was observed in this case. Hunter pointed out that the planarity of the arene ring can be distorted by a substituent [5]. An inward distortion, $\delta d < 0$, will take place when the substituent is an electron-withdrawing group. On the other hand, an outward distortion, $\delta d > 0$ [6], is expected for an electron-donating substituent. The above rule is obeyed unless a very bulky substituent is present. In our case, $\delta d > 0$ for both Cr(1)—C(17) and Cr(1)—C(14). The former is due to the electron-donating ability of —$CH_3$ [7]. The latter is due to the resonance of conjugated multiple bonds of benzene and cyclopentadiene rings thus acts as a $\pi$ electron-donating group. Accordingly, outward distortion was found.

The reaction of (1) with indenyl lithium was carried out under the same reaction conditions mentioned above (Scheme 2). 3-[Tricarbonyl($\eta^6$-4-toluene) chromium]indene (4) was observed as the only isolatable product. The characterization of this compound was achieved by $^1H$, $^{13}C$ NMR, IR and mass spectra. $^1H$ NMR shows a $CH_2$ peak besides other corresponding peaks thus ruling out the possibility of forming (4'). The structure of (4) was further determined by X-ray diffraction (Fig. 2). The bond lengths of C(10)—C(11) and C(11)—C(12) are 1.357 and 1.494 Å, respectively. The former is a typical double bond, while the latter is a typical single bond (Table 3). The conformation of the observed product results from a 1,3-hydrogen shift after the direct attack of (1) by indenyl. A 1,2-hydrogen shift is unlikely here because of the lack of a proper position for placing two double bonds in the cyclopentadiene ring of the



**(1)**                              **(2')**                              **(2)**



**(3)**
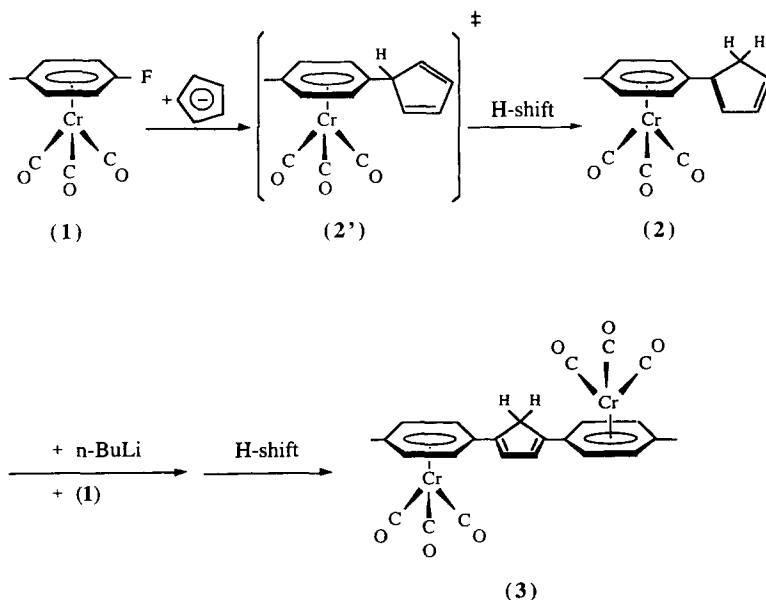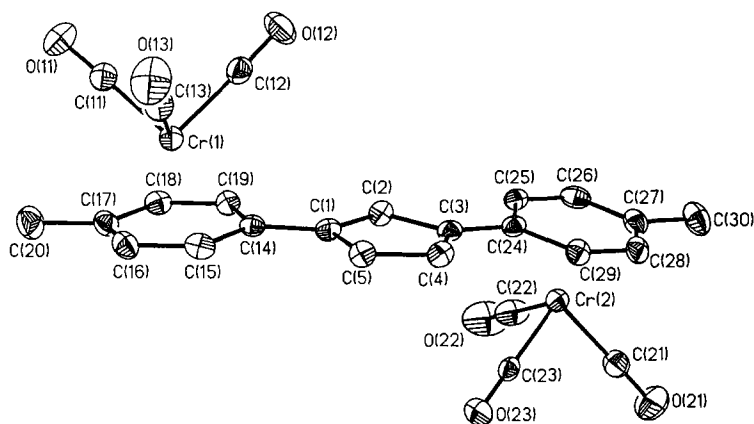
Scheme 1.

Fig. 1. ORTEP drawing with the numbering scheme of **3**. Hydrogen atoms were omitted for clarity.

Table 1. Crystal data of **3**, **4**, and **7**

| Formula | $C_{25}H_{18}Cr_2O_6$ | $C_{19}H_{14}CrO_3$ | $C_{33}H_{22}Cr_2O_6$ |
|---|---|---|---|
| Formula weight | 518.4 | 342.3 | 618.5 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ |
| $a(\text{Å})$ | 11.291(2) | 6.685(1) | 9.072(1) |
| $b(\text{Å})$ | 7.392(1) | 9.584(2) | 9.537(2) |
| $c(\text{Å})$ | 26.963(3) | 12.559(1) | 16.762(1) |
| $\alpha(°)$ | | 99.87(1) | 103.32(1) |
| $\beta(°)$ | 92.96(1) | 96.75(1) | 95.95(1) |
| $\gamma(°)$ | | 92.09(1) | 100.61(1) |
| $V(\text{Å}^3)$ | 2247.4(5) | 785.9(2) | 1370.8(5) |
| $Z$ | 4 | 2 | 2 |
| $D_c(\text{g cm}^{-3})$ | 1.532 | 1.446 | 1.498 |
| $\lambda(\text{Mo-}K_\alpha)(\text{Å})$ | 0.71073 | 0.71073 | 0.71073 |
| $\mu(\text{mm}^{-1})$ | 1.006 | 0.739 | 0.839 |
| Range (°) | 4.0 to 48.0 | 4.0 to 50.0 | 4.0 to 50.0 |
| Scan type | $2\theta/\theta$ | $2\theta/\theta$ | $2\theta/\theta$ |
| No. of reflections collected | 4020 | 2907 | 4995 |
| No. of independent reflections | 3500 ($R_{int} = 2.57\%$) | 2664($R_{int} = 1.83\%$) | 4672($R_{int} = 2.05\%$) |
| No. of observe reflections | 2678($F > 4.0\sigma(F11)$) | 2529($F > 4.0\sigma(F\text{ff}11)$) | 3978($F > 4.0\sigma(F11)$) |
| No. of refined parameters | 298 | 208 | 370 |
| $R_f{}^a$ for significant reflections | 0.0438 | 0.0344 | 0.0474 |
| $R_w{}^b$ for significant reflections | 0.0649 | 0.0643 | 0.0750 |
| $GoF^c$ | 1.17 | 1.82 | 1.42 |

$^a R_f = [\Sigma(F_0 - F_c)/\Sigma F_0]$.
$^b R_w = \Sigma w^{1/2}(F_0 - F_c)/\Sigma w^{1/2}F_0$.
$^c GoF = [\Sigma w(F_0 - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$. $W^{-1} = \sigma^2(F11) + 0.0010F^2$.

indene without causing the destruction of the aromaticity. The dihedral angle between arene and indenyl rings is 46°. It is far away from the expected smaller dihedral angle, which might gain better electron delocalization energy. Again, it might be a result of the compromise between crystal packing force and the electronic effect for this compound in the solid state. In this case, again we see that $\delta d > 0$ for Cr—C(7) and Cr—C(4). 1,3-Bis[tricarbonyl($\eta^6$-4-toluene) chromium]indene (**5**) was obtained from the reaction of (**1**) with deprotonated (**4**). It was characterized by $^1$H NMR, $^{13}$C NMR, IR, and mass spectra. Unfortunately, attempts to grow crystals were not successful

partly due to its poor solubility in many solvents. The fact that two distinct —$CH_3$ peaks were observed for (**5**) in $^1$H NMR was noteworthy. One might expect a fluxional behaviour of the geminal proton taking place in this case and therefore the two —$CH_3$ peaks would not be differentiated in the $^1$H NMR.

The reaction of (**1**) with a cyclopentadienyl related carbanion, fluorenyl lithium, was carried out (Scheme 3). 9-[Tricarbonyl($\eta^6$-4-toluene)chromium] fluorene (**6**) was obtained as the only separated product. The structure was confirmed by the X-ray crystallography [8]. Since only one position is available for the attack in substitution plus the proton shift is not possible in

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**

| | | | |
|---|---|---|---|
| Cr(1)—C(11) | 1.836(5) | Cr(1)—C(12) | 1.831(5) |
| Cr(1)—C(13) | 1.831(5) | Cr(1)—C(14) | 2.263(4) |
| Cr(1)—C(15) | 2.224(5) | Cr(1)—C(16) | 2.225(5) |
| Cr(1)—C(17) | 2.237(5) | Cr(1)—C(18) | 2.218(4) |
| Cr(1)—C(19) | 2.209(4) | Cr(2)—C(21) | 1.841(5) |
| Cr(2)—C(22) | 1.846(6) | Cr(2)—C(23) | 1.841(5) |
| Cr(2)—C(24) | 2.237(4) | Cr(2)—C(25) | 2.218(4) |
| Cr(2)—C(26) | 2.227(5) | Cr(2)—C(27) | 2.240(5) |
| Cr(2)—C(28) | 2.204(5) | Cr(2)—C(29) | 2.207(4) |
| C(1)—C(2) | 1.498(6) | C(1)—C(5) | 1.355(6) |
| C(1)—C(14) | 1.473(6) | C(2)—C(3) | 1.500(6) |
| C(3)—C(4) | 1.344(6) | C(3)—C(24) | 1.468(6) |
| C(4)—C(5) | 1.457(6) | C(11)—O(11) | 1.156(6) |
| C(12)—O(12) | 1.156(7) | C(13)—O(13) | 1.163(6) |
| C(17)—C(20) | 1.517(7) | C(21)—O(21) | 1.150(7) |
| C(22)—O(22) | 1.139(8) | C(23)—O(23) | 1.150(6) |
| C(27)—C(30) | 1.513(7) | | |
| C(2)—C(1)—C(5) | 108.5(4) | C(1)—C(2)—C(3) | 103.5(3) |
| C(2)—C(3)—C(4) | 109.1(4) | C(3)—C(4)—C(5) | 109.3(4) |
| C(1)—C(5)—C(4) | 109.6(4) | Cr(1)—C(11)—O(11) | 178.7(4) |
| Cr(1)—C(12)—O(12) | 179.1(5) | Cr(1)—C(13)—O(13) | 179.4(5) |
| C(1)—C(14)—C(15) | 121.4(4) | C(1)—C(14)—C(19) | 121.1(3) |



**(1)**          **(4')**          **(4)**



**(5)**
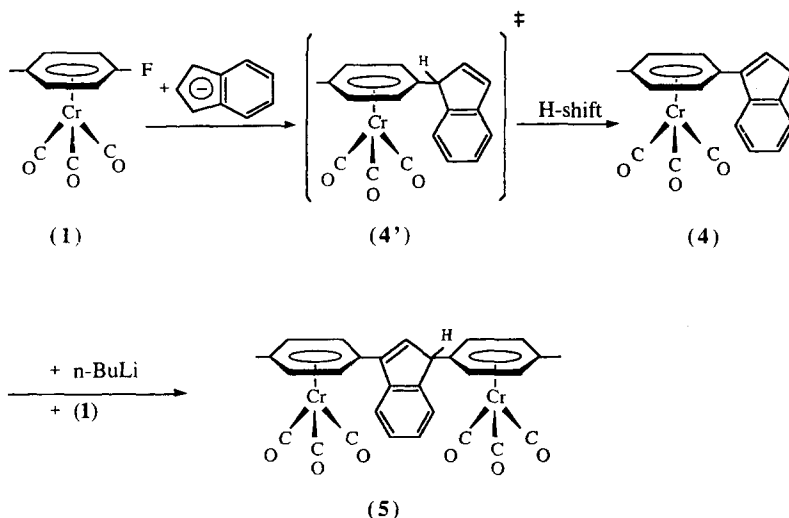
Scheme 2.

this case, thereby, only the direct attached product was found and no hydrogen shift was observed.

Further reaction of (**1**) with deprotonated (**6**) resulted in the formation of 9,9-bis[tricarbonyl($\eta^6$-4-toluene)chromium]fluorene (**7**) (Scheme 4). The fact that the yield of the formation of (**7**) is lower than that of (**5**), 25% *vs* 35%, is attributed to the steric effect. (**7**) was characterized by $^1$H, $^{13}$C NMR, IR and mass spectra. Fortunately, we were able to grow single crystals of (**7**) and the structure was determined by X-ray diffraction even though the solubility of (**7**) in many solvents was poor (Fig. 3). An expected symmetrical geometry, $C_{2v}$ symmetry, was not observed in the solid state structure. Nevertheless, the fact that

only one —CH$_3$ peak was observed in the $^1$H NMR demonstrates that the two areneCr(CO)$_3$ fragments rotate freely in solution therefore exhibiting the equivalency of these two —CH$_3$ peaks on the NMR time scale. In this case, $\delta d > 0$ for Cr(1)—C(7) as in the previous cases (Table 4). The $\delta d$ for Cr(1)—C(4) is rather small and might be due to the poor resonance of conjugated multiple bonds between arene and fluroene ring under this crowded structure. The organic moiety, 9,9-bis($\eta^6$-4-toluene)fluorene (**8**), was obtained by exposing the CH$_2$Cl$_2$ solution of (**7**) to air. This metal free organic part was further purified and the conversion was almost quantitative. This demonstrates a pathway of making quaternary carbon
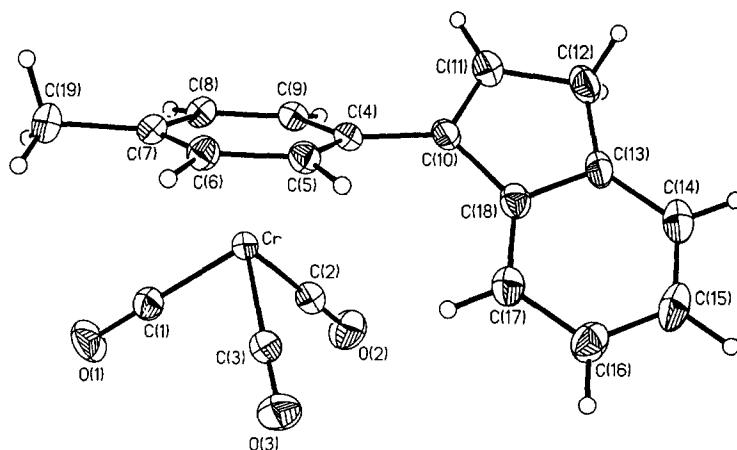
Fig. 2. ORTEP drawing with the numbering scheme of 4. Hydrogen atoms were omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) for 4

| Cr—C(1) | 1.833(2) | Cr—C(2) | 1.840(3) |
|---|---|---|---|
| Cr—C(3) | 1.831(2) | Cr—C(4) | 2.264(2) |
| Cr—C(5) | 2.216(2) | Cr—C(6) | 2.223(2) |
| Cr—C(7) | 2.248(2) | Cr—C(8) | 2.233(2) |
| Cr—C(9) | 2.225(2) | C(1)—O(1) | 1.157(3) |
| C(2)—O(2) | 1.153(3) | C(3)—O(3) | 1.156(3) |
| C(4)—C(5) | 1.408(3) | C(4)—C(9) | 1.409(3) |
| C(4)—C(10) | 1.473(3) | C(5)—C(6) | 1.419(3) |
| C(6)—C(7) | 1.411(3) | C(7)—C(8) | 1.410(4) |
| C(7)—C(19) | 1.507(4) | C(8)—C(9) | 1.407(3) |
| C(10)—C(11) | 1.357(4) | C(10)—C(18) | 1.478(3) |
| C(11)—C(12) | 1.494(3) | C(12)—C(13) | 1.502(4) |
| C(13)—C(14) | 1.398(3) | C(13)—C(18) | 1.406(3) |
| C(14)—C(15) | 1.369(4) | C(15)—C(16) | 1.396(4) |
| C(16)—C(17) | 1.392(3) | C(17)—C(18) | 1.387(3) |
| C(5)—C(4)—C(9) | 117.6(2) | C(6)—C(7)—C(8) | 118.3(2) |
| C(4)—C(10)—C(11) | 123.4(2) | C(4)—C(10)—C(18) | 127.4(2) |
| C(11)—C(10)—C(18) | 109.2(2) | C(10)—C(11)—C(12) | 110.8(2) |
| C(11)—C(12)—C(13) | 103.1(2) | C(12)—C(13)—C(18) | 109.5(2) |



(1)                    (6)
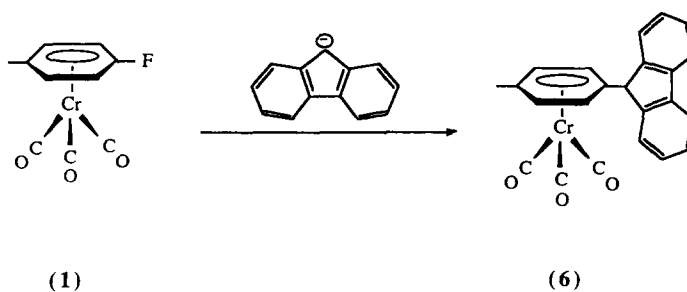
Scheme 3.

which might be difficult to do otherwise. Attempts to make similar compounds, to (7) through the consecutive nucleophilic substitutions of $CH_2Ph_2$ by (1) resulted in failure. However, a closely related but less hindered compound, $Ph_2CH_2[Cr(CO)_3]_2$, was reported by refluxing $CH_2Ph_2$ and $Cr(CO)_6$ in diglyme [9].

In summary, we were able to prepare some chromium-containing bimetallic compounds through consecutive nucleophilic substitution and determined

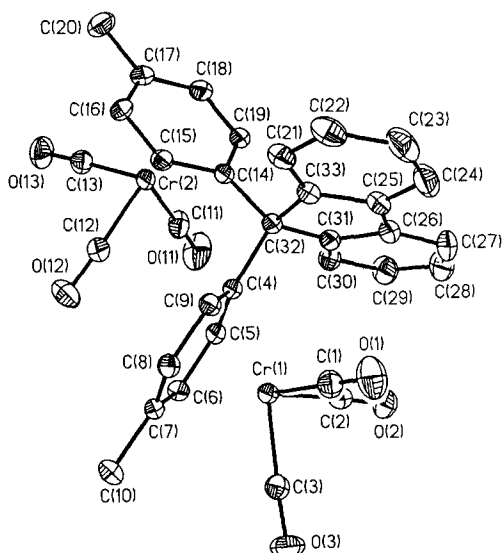**(6)**                                      **(7)**



**(8)**
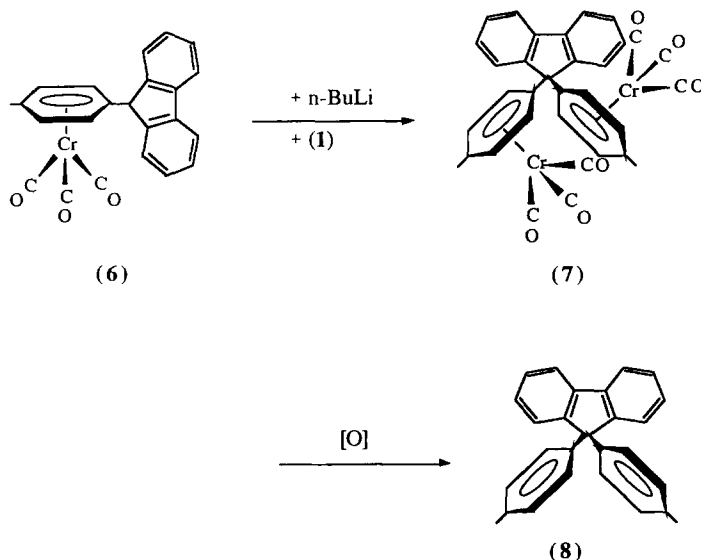
Scheme 4.



Fig. 3. ORTEP drawing with the numbering scheme of 7.
Hydrogen atoms were omitted for clarity.

their structures. We also demonstrated that the
organic moiety of the bimetallic compound (7), which
might be difficult to make from conventional methods,
can be obtained easily under mild oxidation
conditions.

## EXPERIMENTAL

### Apparatus and materials

All operations 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 Centrifugal Thin-Layer

Chromatography (TLC, Chromatotron, Harrison
model 8924). $^1$H and $^{13}$C NMR spectra were recorded
(Varian-300 spectrometer) at 300 and 75.46 MHz,
respectively; chemical shifts are reported in ppm rela-
tive to internal TMS. IR spectra of solution in $CHCl_3$
were recorded on a Hitachi 270–30 spectrometer.
Mass spectra were recorded on JOEL JMS-SX/SX
102A GC/MS/MS spectrometer. Elementary analysis
were recorded on Heraeus CHN-O-S-Rapid.

### General procedure for preparations of 2, 3, 4, 5 and 7

Into a 50 cm$^3$ flask was placed indene (0.07 cm$^3$,
1.06 mmol), which was evacuated under reduced pres-
sure for 10 min and then filled with nitrogen. The
reaction flask was followed by adding 2 cm$^3$ of anhy-
drous tetrahydrofuran and cooled to −78°C (acetone-
N$_{2(l)}$ bath). Next, *n*-BuLi (1.6 M, 0.4 ml, 0.63 mmol)
was added drop by drop to the cold reaction flask.
The deprotonation process was carried out at that
temperature for 1.2 h and then we added HMPA (0.56
cm$^3$, 3.2 mmol). 30 min later, a solution of tricar-
bonyl($\eta^6$-4-fluorotoluene)chromium (1) (0.13 g, 0.53
mmol) in 1.0 cm$^3$ of anhydrous THF was added slowly
to the cold reaction mixture. The reaction was well
stirred at −78°C for another 3 h and gently warmed
to 20°C during the next 16 h.

Subsequently, the resulting yellow solution was fil-
tered through a small amount of silica gel. The filtrate
was evaporated under reduced pressure to yield the
crude product. Purification with centrifugal thin-layer
chromatography (eluent: hexane), a yellow band of
3-[tricarbonyl($\eta^6$-4-toluene)chromium]indene (4) was
isolated (0.13 g, 65.7%). In addition, a small amount
of unreacted (1) was recovered.

2. Yellow crystals in 68.6% yield. $^1$H NMR
(CDCl$_3$): δ 2.19 (s, 3H, Me), 3.23 (d, $J$ = 1.2 Hz, 2H,

Table 4. Selected bond lengths (Å) and bond angles (°) for **7**

| | | | |
|---|---|---|---|
| Cr(1)—C(1) | 1.836(4) | Cr(1)—C(2) | 1.840(4) |
| Cr(1)—C(3) | 1.846(4) | Cr(1)—C(4) | 2.235(3) |
| Cr(1)—C(5) | 2.213(3) | Cr(1)—C(6) | 2.227(3) |
| Cr(1)—C(7) | 2.250(3) | Cr(1)—C(8) | 2.234(3) |
| Cr(1)—C(9) | 2.201(3) | C(1)—O(1) | 1.150(5) |
| C(2)—O(2) | 1.160(5) | C(3)—O(3) | 1.149(5) |
| C(4)—C(5) | 1.420(5) | C(4)—C(9) | 1.406(5) |
| C(4)—C(32) | 1.555(5) | C(5)—C(6) | 1.416(5) |
| C(6)—C(7) | 1.406(5) | C(7)—C(8) | 1.404(5) |
| C(7)—C(10) | 1.506(5) | C(8)—C(9) | 1.422(5) |
| C(21)—C(22) | 1.384(6) | C(21)—C(33) | 1.384(6) |
| C(22)—C(23) | 1.394(6) | C(23)—C(24) | 1.367(8) |
| C(24)—C(25) | 1.383(6) | C(25)—C(26) | 1.457(6) |
| C(25)—C(33) | 1.401(4) | C(26)—C(27) | 1.402(6) |
| C(26)—C(31) | 1.401(4) | C(27)—C(28) | 1.367(8) |
| C(28)—C(29) | 1.371(6) | C(29)—C(30) | 1.388(6) |
| C(30)—C(31) | 1.392(6) | C(31)—C(32) | 1.530(5) |
| C(32)—C(33) | 1.538(5) | | |
| C(4)—C(32)—C(14) | 109.2(2) | C(4)—C(32)—C(31) | 110.9(3) |
| C(14)—C(32)—C(31) | 114.7(3) | C(4)—C(32)—C(33) | 110.6(3) |
| C(14)—C(32)—C(33) | 109.8(3) | C(31)—C(32)—C(33) | 101.4(2) |
| C(21)—C(33)—C(25) | 120.2(3) | C(21)—C(33)—C(32) | 130.0(3) |
| C(25)—C(33)—C(32) | 109.7(3) | C(24)—C(25)—C(26) | 130.9(4) |
| C(24)—C(25)—C(33) | 120.1(4) | C(26)—C(25)—C(33) | 108.9(3) |

CH$_2$ in cyclopentadienyl), 5.26 (d, $J = 6.9$ Hz, 2H, areneCr(CO)$_3$), 5.67 (d, $J = 6.9$ Hz, 2H, arene-Cr(CO)$_3$), 6.48 (m, 2H, arene in cyclopentadienyl), 6.79 (d, $J = 0.6$ Hz, 1H, arene in cyclopentadienyl); $^{13}$C NMR (CDCl$_3$): $\delta$ 20.371 (1C, Me), 40.932 (1C, CH$_2$, in cyclopentadienyl), 91.259, 92.710, 92.884, 93.022 (1C, areneCr(CO)$_3$), 102.590, 107.988 (1C, *ipso* of areneCr(CO)$_3$), 129.499, 132.721, 133.976 (1C, arene in cyclopentadienyl), 142.103 (1C, *ipso* of arene in cyclopentadienyl), 233.704 (3C, 3CO); IR(CHCl$_3$): $v_{(CO)}$ 1888, 1966 cm$^{-1}$; MS $m/z$ 292(P$^+$).

**3**. Red crystals in 45.8% yield. $^1$H NMR (CDCl$_3$): $\delta$ 2.21 (s, 6H, Me), 3.45 (s, 2H, CH$_2$, arene in cyclopentadienyl), 5.28 (d, $J = 1.2$ Hz, 4H, areneCr(CO)$_3$), 5.68 (d, $J = 1.2$ Hz, 4H, areneCr(CO)$_3$), 6.74 (d, $J = 1.8$ Hz, 2H, CH, arene in cyclopentadienyl); $^{13}$C NMR (CDCl$_3$): $\delta$ 20.415 (2C, Me), 40.060 (1C, CH$_2$, in cyclopentadienyl), 91.268, 92.808 (4C, arene-Cr(CO)$_3$), 100.881, 108.207 (2C, *ipso* of arene-Cr(CO)$_3$), 129.241 (2C, arene in cyclopentadienyl), 142.325 (2C, *ipso* of arene in cyclopentadienyl), 233.473 (6C, 6CO); IR(CHCl$_3$): $v_{(CO)}$ 1894, 1968 cm$^{-1}$; MS $m/z$ 518 (P$^+$).

**4**. Yellow crystals in 65.7% yield. $^1$H NMR (CDCl$_3$): $\delta$ 2.25 (s, 3H, Me), 3.51 (d, $J = 1.5$ Hz, 2H, CH$_2$ in indenyl), 5.30 (d, $J = 6.6$ Hz, 2H, arene-Cr(CO)$_3$), 5.76 (d, $J = 6.6$ Hz, 2H, areneCr(CO)$_3$), 7.32 (m, 2H, arene in indenyl), 7.51 (d, $J = 6.9$ Hz, 1H, arene in indenyl), 7.60 (d, $J = 7.5$ Hz, 1H, arene in indenyl); $^{13}$C NMR (CDCl$_3$): $\delta$ 20.415 (1C, Me), 38.137 (1C, CH$_2$, in indenyl), 92.639, 93.983 (1C, areneCr(CO)$_3$), 102.688, 108.439 (1C, *ipso* of arene-Cr(CO)$_3$), 120.046, 124.291, 125.413, 126.437, 134.092

(1C, arene in indenyl), 140.394, 142.556, 144.453, (1C, *ipso* of arene in indenyl), 233.313 (3C, 3CO); IR(CHCl$_3$): $v_{(CO)}$ 1886, 1970 cm$^{-1}$; MS $m/z$ 343(P$^+$).

**5**. Yellow crystals in 34.9% yield. $^1$H NMR (CDCl$_3$): $\delta$ 2.17 (s, 3H, Me), 2.27 (s, 3H, Me), 4.32 (d, $J = 3.3$ Hz, 1H, CH in indenyl), 5.44 (m, 8H, areneCr(CO)$_3$), 6.76 (d, $J = 3.3$ Hz, 1H, arene in indenyl), 7.43 (d, $J = 12.0$ Hz, 2H, arene in indenyl), 7.66 (d, $J = 12.0$ Hz, 2H, arene in indenyl); $^{13}$C NMR (CDCl$_3$): $\delta$ 20.335 (1C, Me), 20.460 (1C, Me), 92.310, 92.648, 92.870, 93.075 (1C, areneCr(CO)$_3$), 93.209 (2C, areneCr(CO)$_3$), 93.342, 95.220 (1C, arene-Cr(CO)$_3$), 106.730, 108.394, 109.553 (1C, *ipso* of areneCr(CO)$_3$), 121.069, 124.131, 126.606, 127.941, 136.744 (1C, arene in indenyl), 141.266, 141.497, 146.847 (1C, *ipso* of arene in indenyl), 233.072, 233.526 (3C, 3CO); IR(CDCl$_3$): $v_{(CO)}$ 1898, 1974 cm$^{-1}$; MS $m/z$ 568 (P$^+$).

**7**. Yellow crystals in 24.6% yield. $^1$H NMR (CDCl$_3$): $\delta$ 2.16 (s, 6H, Me), 4.90 (d, $J = 5.1$ Hz, 4H, areneCr(CO)$_3$), 5.64 (d, $J = 5.1$ Hz, 4H, arene-Cr(CO)$_3$), 7.58 (m, 4H, arene in fluorenyl), 7.66 (d, $J = 6.0$ Hz, 2H, arene in fluorenyl), 7.79 (d, $J = 6.0$ Hz, 4H, arene in fluorenyl); $^{13}$C NMR (CDCl$_3$): $\delta$ 20.282 (2C, Me), 59.082 (1C, C in fluorenyl), 89.533, 95.897 (4C, areneCr(CO)$_3$), 110.317, 111.171 (2C, *ipso* of areneCr(CO)$_3$), 121.016, 125.911, 127.407, 129.134 (2C, arene in fluorenyl), 140.242, 147.755 (2C, *ipso* of arene in fluorenyl)Cr(CO)$_3$), 232.467 (6C, 6CO); IR(CHCl$_3$): $v_{(CO)}$ 1900, 1972 cm$^{-1}$; MS $m/z$ 618 (P$^+$);

Found: C, 64.3; H, 3.4. Calc. for C$_{33}$H$_{22}$Cr$_2$O$_6$: C, 64.1; H, 3.6%.

*Preparation of* **8**

Into a 50 cm³ flask was placed (**7**) (0.20 g, 0.32 mmol) and 20 cm³ of CH₂Cl₂. The solution was exposed to air and sunlight for about 20 min. The green precipitate was separated and the filtrate was passed through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent: hexane), a colorless band of (**8**) was isolated (0.11 g, 0.31 mmol). The yield of (**8**) is 98.2%.

**8**. ¹H NMR (CDCl₃): δ 2.20 (s, 6H, Me), 7.30 (m, 16H, arene in fluorenyl and toluenyl); ¹³C NMR (CDCl₃): δ 20.888 (2C, Me), 64.808 (1C, C in fluorenyl), 120.109, 126.094, 127.325, 127.704 (4C, arene in fluorenyl), 128.040, 128.903 (2C, arene in toluenyl), 136.172, 140.106 (2C, *ipso* of toluenyl), 143.083, 151.573 (2C, *ipso* of arene in fluorenyl); MS *m/z* 346 (P⁺).

*Crystal structure determination of* **3, 4, 7**

Orange plate crystal of **3, 4** and a yellow parallelpiped crystal of **7** with size of 0.2 × 0.4 × 0.6 mm, 0.4 × 0.7 × 0.7 mm and 0.3 × 0.4 × 0.4 mm, respectively, were used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo-$K_\alpha$ radiation, $\lambda = 0.71073$ Å. The positions of heavy atoms in the structures 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 0.96 Å, and the temperature factors were fixed at 0.08 Å. 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 Micro VAX 3100 computer.

The crystallographic data of the complex **3, 4, 7** are summarized in Table 1.

*Supplementary Material Available*

Atomic coordinates of **3, 4,** and **7**, tables of thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates have been deposited as supplementary material.

**REFERENCES**

1.  (a) L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*. University Science Books, Mill Valley, CA (1994); (b) 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); (c) R. Davis and L. A. P. Kane-Maguire, in *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel) Vol. 3, p. 953. Pergamon Press, Oxford (1982) and references cited therein; (d) W. E. Watts, in *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel) Vol. 8, p. 1013. Pergamon Press, Oxford (1982); (e) H. M. Colguhoun, J. Holton, D. J. Thompson and M. V. Twigg, *New Pathways for Organic Sythesis: Practical Applications of Transition Metals*. Plenum Press, New York (1984); (f) E. P. Kündig, N. P. Do Thi, P. Paglia, D. P. Simmons, S. Spichiger and E. Wenger, in *Organometallics in Organic Synthesis* (Edited by A. de Meijere and T. Dieck) Vol. 1. Springer-Verlag, Berlin, Heidelberg (1988); (g) K. Schlögl, in *Organometallics in Organic Synthesis* (Edited by A. de Meijere and T. Dieck) Vol. 2. Springer-Verlag, Berlin, Heidelberg (1988); (h) A. Solladie Cavallo, *Polyhedron* 1985, **4**, 901.
2.  (a) D. A. Roberts and G. L. Geoffroy, in *Comprehensive Organometallic Chemistry*, (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel) Chap. 40. Pergamon Press, Oxford (1982); (b) R. M. Bullock and C. P. Casey, *Acc. Chem. Res.* 1987, **20**, 167.
3.  (a) Y. K. Kang, Y. K. Chung and S. W. Lee, *Organometallics* 1995, **14**, 4905; (b) Z. V. Todres and E. A. Ionina, *J. Organomet. Chem.* 1993, **453**, 197; (c) H. Plenio, *Organometallics* 1992, **11**, 1856; (d) S. P. Gubin and V. S. Khandkarova, *J. Organomet. Chem.* 1970, **22**, 449; (e) L. D. Schulte and R. D. Rieke, *J. Org. Chem.* 1987, **52**, 4829.; (f) E. W. Neuse, *J. Organomet. Chem.* 1972, **40**, 387.
4.  (a) V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Tetrahedron* 1963, **19**, 1939; (b) W. R. Roth, *Tetrahedron Lett.* 1964, **17**, 1009; (c) S. McLean and P. Haynes, *Tetrahedron Lett.* 1964, **34**, 2385; (d) A. Ceccon, A. Gambaro, F. Gorttardi, F. Mannoli and A. Venzo, *J. Organomet. Chem.* 1989, **363**, 91; (e) J. M. E. Krekels, J. W. de Haan and H. Kloosterziel, *Tetrahedron Lett.* 1970, **32**, 2751.
5.  (a) A. D. Hunter, L. Shilliday, W. S. Furey, and M. J. Zaworotko *Organometallics* 1992, **11**, 1550; (b) J. Li, A. D. Hunter, R. McDonald, B. D. Santarsiero, S. G. Bott and J. L. Atwood, *Organometallics* 1992, **11**, 3050.
6.  The parameter $\delta d$ is defined as the difference between the Cr—$C_{ipso}$ bond length and the average of the other Cr—C(H) bond lengths. $\delta d = d\text{Cr}—C_{ipso} - d\text{Cr}—C(H)_{av}$.
7.  G. M. Bodner and L. J. Todd, *Inorg. Chem.* 1974, **13**, 360.
8.  F.-E Hong, S.-C. Lo, M.-W. Liou, L.-F. Chou and C.-C. Lin, *J. Organomet. Chem.* 1996, **516**, 123.
9.  E. Kolehmainen, K. Laihia, J. Korvola, V. S. Kaganovich, M. I. Rybinskaya and Z. A. Kerzina, *J. Organomet. Chem.* 1995, **485**, 109.