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Studies on olefin-coordinating transition metal carbene complexes

XIX *. Synthesis and structural characterization of the cycloalkene ligated carbonyl-chromium and -tungsten carbene complexes

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Abstract

Reaction of norbornadiene(tetracarbonyl)-chromium (**1**) and -tungsten (**2**) with aryllithium reagents, ArLi (Ar = C_6H_5, *o*-,*m*-,*p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$), in ether at low temperature, and subsequent alkylation of the acylmetalate intermediates formed with Et_3OBF_4 in aqueous solution at 0°C gave seven crystalline complexes with the compositions $C_7H_8(CO)_3CrC(OC_2H_5)Ar$ (**4–9**) and $C_7H_8(CO)_3WC(OC_2H_5)Ar$ (**10**) formulated as norbornadiene(tricarbonyl)[ethoxy(aryl)carbene]-chromium and -tungsten complexes, respectively. Complex **7** has been characterized by X-ray diffraction. Complex **7** is orthorhombic, space group $P2_12_12_1$ with $a = 10.372(3)$, $b = 12.093(6)$, $c = 14.154(9)$ Å, $V = 1775.27$ Å^3, and $Z = 4$, final $R = 0.0529$ and $R_w = 0.0562$ for 1385 observed reflections. The 1,5-cyclooctadiene(tetracarbonyl)tungsten compound (**3**) reacts similarly to give analogous carbene complexes $C_8H_{12}(CO)_3WC(OC_2H_5)Ar$ (**11–13**).

Introduction

In recent years, the syntheses and structural characterizations of olefin-coordinated transition metal carbene complexes and/or their isomerized products have been studied extensively in our laboratory [1–10]. Several novel isomerization reactions of olefin ligands have been observed and a series of isomerized carbene complexes with novel structure has been isolated.

Previously, we reported on the reaction of norbornadiene(tricarbonyl)iron and 1,5-cyclooctadiene(tricarbonyl)iron with aryllithium reagents at low temperature,

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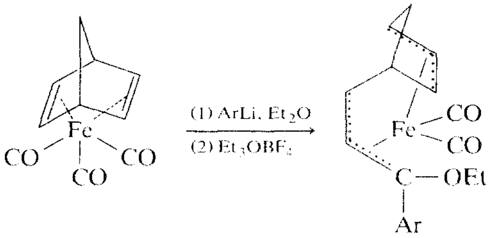
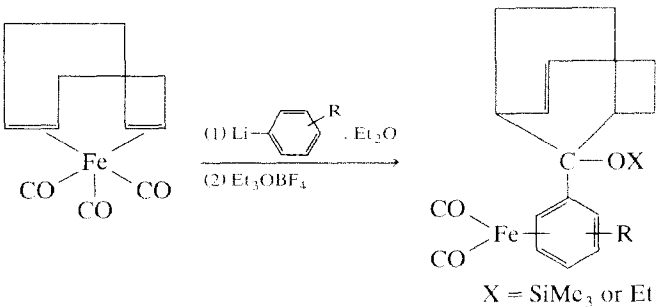
followed by alkylation of the acylmetalate intermediates formed with Et_3OBF_4 to give novel ring-opened diallyliron complexes [5] (eq. 1) and (η^6-arene)dicarbonyliron complexes [8] (eq. 2), respectively.



(1)



(2)

We have also reported on the reaction of norbornadiene(tetracarbonyl)molybdenum with aryllithium reagents and subsequent alkylation of the acylmetalates formed with Et_3OBF_4 to give normal olefin-coordinated carbene complexes, norbornadiene(tricarbonyl)[ethoxy(aryl)carbene]molybdenum complexes [11]. In an extension of our research, we chose norbornadiene(tetracarbonyl)-chromium (**1**) and -tungsten (**2**), and 1,5-cyclooctadiene(tetracarbonyl)-tungsten, (1,5-COD)$W(CO)_4$ (**3**) as the starting materials in order to further investigate the effect of different cycloalkene ligands and different central metals on the reaction products.

Several norbornadiene(tricarbonyl)[ethoxy(aryl)carbene]-chromium and -tungsten, and 1,5-cyclooctadiene(tricarbonyl)[ethoxy(ary)carbene]-tungsten complexes were obtained by the reaction of compounds **1**, **2** and **3** with aryllithium in a similar manner as previously described [1,5,11]. Here, we report on the synthesis and crystal X-ray structural determination of these new complexes.

Experimental

General procedure

All manipulations were carried out under a nitrogen atmosphere in reagent grade solvents by using standard Schlenk techniques. Solvents used were distilled under nitrogen from the following drying agents: diethyl ether from sodium benzophenone ketyl, petroleum ether (30–60°C) from CaH_2, and CH_2Cl_2 from P_2O_5. The solvents were stored over 4-Å molecular sieves under nitrogen prior to use. The neutral alumina (Al_2O_3) used for chromatography was deoxygenated at room temperature in a high vacuum for 16 h, deactivated with 5% w/w nitrogen-saturated water, and stored under nitrogen. Norbornadiene(tetracarbonyl)-chromium (**1**) [12] and -tungsten (**2**) [13], 1,5-cyclooctadiene(tetracarbonyl)-tungsten, (1,5-COD)W(CO)$_4$ (**3**) [13], Et_3OBF_4 [14], and aryllithium reagents [15–19] were prepared by literature methods.

IR, ^{1}H NMR and mass spectra were recorded on a Zeiss Specord-75 spectrophotometer, a Varian XL-200 spectrometer, and a Finnigan 4021/MS/DS spectrometer, respectively. The melting points were determined in sealed, nitrogen-filled capillaries and are not corrected.

1. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_5$ (4). To a solution of 0.030 g (1.17 mmol) of **1** in 60 ml of ether was added dropwise 1.30 mmol of C_6H_5Li [15] in 10 ml of ether at -70°C within 15 min. The reaction mixture was stirred at -65–60°C for 3 h during which time the yellow solution gradually turned dark-red. After removal of the solvent in a high vacuum at -50°C, to the dark-red solid residue obtained was added Et_3OBF_4 [14] (*ca.* 1 g). This solid mixture was dissolved in 20 ml of nitrogen-saturated water at 0°C with vigorous stirring and the mixture was covered with petroleum ether (30–60°C). Immediately afterwards, Et_3OBF_4 was added portionwise, with strong stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na_2SO_4. After vacuum removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) at -20°C with petroleum ether as the eluant. The red band was eluted and collected. The solvent was removed *in vacuo* and the residue was recrystallized from petroleum ether/ CH_2Cl_2 solution at -80°C to give 0.24 g (50%, based on **1**) of orange-red crystals of **4**, m.p. 45–46°C (decomp.). Anal. Found: C, 62.75; H, 4.82; Cr, 11.28. $C_{19}H_{18}O_4Cr$ (362.35) calc.: C, 62.98; H, 5.01; Cr, 11.35%. m/z: 362 (M^+), 334 (M^+- CO), 306 (M^+- 2CO), 278 (M^+- 3CO).

2. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CH_3$-o (5). Similar to the preparation of **4**, the reaction of 0.40 g (1.56 mmol) of **1** with 1.70 mmol of o-$CH_3C_6H_4Li$ [16] at -60–45°C for 4 h, followed by alkylation and further treatment gave 0.29 g (50%, based on **1**) of **5** as red crystals, m.p. 70–71°C (decomp.). Anal. Found: C, 63.95; H, 5.42; Cr, 13.11. $C_{20}H_{20}O_4Cr$ (376.38) calc.: C, 63.82; H, 5.36; Cr, 13.82%. m/z: 376 (M^+), 348 (M^+- CO), 320 (M^+- 2CO), 292 (M^+- 3CO).

3. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CH_3$-m (6). The reaction of 0.40 g (1.56 mmol) of **1** with 1.70 mmol of m-$CH_3C_6H_4Li$ [16] was as described in (1) at -65–50°C for 3.5 h. The subsequent alkylation and treatment as described for the preparation of **4** gave 0.28 g (48%, based on **1**) of orange-red crystals of **6**, m.p. 43–44°C (decomp.). Anal. Found: C, 63.85; H, 5.16; Cr, 14.06. $C_{20}H_{20}O_4Cr$ (376.38) calc.: C, 63.82; H, 5.36; Cr, 13.82%. m/z: 376 (M^+), 320 (M^+- 2CO), 292 (M^+- 3CO).

4. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CH_3$-p (7). Compound **1** (0.40 g, 1.56 mmol) was treated with 1.70 mmol of p-$CH_3C_6H_4Li$ [16] at -70–60°C for 3.5 h, followed by alkylation and further treatment as described above for **4** to yield 0.26 g (44%, based on **1**) of red crystalline **7**, m.p. 52–53°C (decomp.). Anal. Found: C, 64.08;, H, 5.40; Cr, 13.30. $C_{20}H_{20}O_4Cr$ (376.38) calc.: C, 63.82; H, 5.36; Cr, 13.82%. m/z: 376 (M^+), 320 (M^+- 2CO), 292 (M^+- 3CO).

5. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4OCH_3$-p (8). n-$C_4H_9Li$ (1.82 mmol) [17] was mixed with a solution of 0.24 g (1.82 mmol) of p-$CH_3OC_6H_4Br$ in 20 ml of ether. The mixture was stirred at room temperature for 1 h. The resulting ether solution of p-$CH_3OC_6H_4Li$ [18] was treated with 0.40 g (1.56 mmol) of **1** in

30 ml of ether at -70–50°C for 3 h. Further treatment in a similar manner as described in the preparation of **4** afforded 0.33 g (54%, based on **1**) of **8** as orange-red crystals, m.p. 60–61°C (decomp.). Anal. Found: C, 61.29; H, 5.20; Cr, 13.25. $C_{20}H_{20}O_5Cr$ (392.38) calc.: C, 61.22; H, 5.14; Cr, 13.25%. *m/z*: 392 (M^+), 364 ($M^+ - CO$), 308 ($M^+ - 3CO$).

6. Preparation of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CF_3$-p *(9).* Compound **1** (0.40 g, 1.56 mmol) was treated, in a similar manner to that described in (1), with fresh p-$CF_3C_6H_4Li$ [19] prepared by the reaction of 0.40 g (1.78 mmol) of p-$CF_3C_6H_4Br$ with 1.78 mmol of n-C_4H_9Li, in ether solution at -70–50°C for 3 h to give 0.41 g (61%, based on **1**) of red crystals of **9**, m.p. 30–31°C (decomp.). Anal. Found: C, 55.78; H, 3.85; Cr, 11.65. $C_{20}H_{17}F_3O_4Cr$ (430.35) calc.: C, 55.82; H, 3.98; Cr, 12.08%. *m/z*: 430 (M^+), 346 ($M^+ - 3CO$).

7. Preparation of $C_7H_8(CO)_3WC(OC_2H_5)C_6H_4CH_3$-o *(10).* Similar to that described in (1), 0.40 g (1.03 mmol) of **2** in ether (50 ml) was treated with o-$CH_3C_6H_4Li$ (1.15 mmol) at -60–50°C for 3 h. The subsequent alkylation and further treatment as described for the preparation of **4** gave 0.32 g (62%, based on **2**) of orange-red crystals of **10**, m.p. 85–86°C (decomp.). Anal. Found: C, 47.34; H, 4.02. $C_{20}H_{20}O_4W$ (508.23) calc.: C, 47.27; H, 3.97%. *m/z*: 508 (M^+), 480 ($M^+ - CO$), 424 ($M^+ - 3CO$).

8. Preparation of $C_8H_{12}(CO)_3WC(OC_2H_5)C_6H_5$ *(11).* To a solution of **3** (0.30 g, 0.75 mmol) in ether (40 ml) at -78°C was added dropwise 1.0 mmol of C_6H_5Li within 15 min. The mixture was stirred at -50–30°C for 3 h during which time the yellow solution gradually turned red. After removal of the solvent in high vacuum at -40°C, the red solid residue was dissolved in 20 ml of nitrogen-saturated water at 0°C and covered with petroleum ether. Immediately afterwards, Et_3OBF_4 was added portionwise, with efficient stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. After evaporation to dryness of the extract *in vacuo*, the residue was chromatographed on Al_2O_3 (neutral) at -20°C with petroleum ether followed by petroleum ether/ether (10:1) as the eluant. The red band was eluted and collected. The solvent was removed in vacuo, and the residue was recrystallized from petroleum ether at -80°C to afford 0.12 g (32%, based on **3**) of red crystals of **11**, m.p. 41–42°C (decomp.). Anal. Found: C, 47.21; H, 4.11. $C_{20}H_{22}O_4W$ (510.25) calc.: C, 47.08; H, 4.35%. *m/z*: 402 ($M^+ - C_8H_{12}$), 374 ($M^+ - CO - C_8H_{12}$), 346 ($M^+ - 2CO - C_8H_{12}$), 268 ($W(CO)_3^+$).

9. Preparation of $C_8H_{12}(CO)_3WC(OC_2H_5)C_6H_4CH_3$-o *(12).* Similar to the procedures described above for the preparation of **11**, the reaction of 0.30 g (0.75 mmol) of **3** with 1.10 mmol of o-$CH_3C_6H_4Li$ at -40–30°C for 4 h, and subsequent alkylation and further treatment gave 0.11 g (28%, based on **3**) of **12** as red crystals, m.p. 52–53°C (decomp.). Anal. Found: C, 47.86; H, 4.45. $C_{21}H_{24}O_4W$ (524.28) calc.: C, 48.11; H, 4.61%. *m/z*: 524 (M^+), 468 ($M^+ - 2CO$), 440 ($M^+ - 3CO$).

10. Preparation of $C_8H_{12}(CO)_3WC(OC_2H_5)C_6H_4OCH_3$-p *(13).* The reaction of 0.30 g (0.75 mmol) of **3** in 40 ml of ether with fresh p-$CH_3OC_6H_4Li$ prepared by the reaction of 0.20 g (1.10 mmol) of p-$CH_3OC_6H_4Br$ with 1.10 mmol of n-C_4H_9Li at -50–30°C for 3 h, followed by alkylation and further treatment similar to the procedures described in (8) gave 0.14 g (36%, based on **3**) of red crystals of **13**, m.p. 60–61°C (decomp.). Anal. Found: C, 46.75; H, 4.10. $C_{21}H_{24}O_5W$

Table 1

IR spectral data of complexes **4–13**

Complex	ν(CO) (cm^{-1})	
	CH_2Cl_2	Hexane
4	1905vs, 1980vs, 2040vs	1930vs, 1996vs, 2023vs
5	1908vs, 1980vs, 2040vs	1918vs, 1983vs, 2010vs
6	1900vs, 1960vs, 2035vs	1906vs, 1988vs, 2020vs
7	1900vs, 1960vs, 2040vs	1920vs, 1987vs, 2020vs
8	1920vs, 1984vs, 2050vs	1920vs, 1986vs, 2020vs
9	1902vs, 1980vs, 2040vs	1918vs, 1990vs, 2020vs
10	1920vs, 1941vs, 2000vs	1915vs, 1936vs, 2007vs
11		1937vs, 1960vs, 2017vs
12		1860vs, 1900vs, 1980vs
13		1883vs, 1940vs, 2006vs

(540.28) calc.: C, 46.68; H, 4.48%. m/z: 540 (M^+), 512 (M^+- CO), 484 (M^+- 2CO), 456 (M^+- 3CO).

Crystal structure determination of 7

Crystals of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CH_3$-*p* (**7**) suitable for X-ray diffraction study were obtained by recrystallization from a petroleum ether/CH_2Cl_2 solution at -80°C. A single crystal of approximate dimensions, $0.25 \times 0.35 \times 0.66$ mm^3 was sealed in capillaries under nitrogen. The X-ray diffraction intensity data of 1842 independent reflections, of which 1385 with $I \geq 2.5\sigma(I)$ were observable, were collected with a Nicolet R 3M/E four-circle diffractometer at -90°C using Mo-K_α radiation with a ω–2θ scan mode within the range $3° \leq 2\theta \leq 42°$. The data were corrected for Lorentz and polarization effects. Complex **7** crystallized in the orthorhombic system. The crystal data: $a = 10.372(3)$, $b = 12.093(6)$, $c = 14.154(9)$ Å, $V = 1775.27$ Å^3, $Z = 4$, $D_c = 1.408$ g/cm^3, and space group $P2_12_12_1$.

The structure was solved by the heavy-atom method. The positional parameter of the Cr atom was determined from the Patterson map. After the position of the Cr atom was determined, the coordinates of the other non-hydrogen atoms were obtained by Fourier synthesis. The positional and anisotropic thermal parameters of the all non-hydrogen atoms were least-squares refined. The coordinates of all hydrogen atoms with isotropic thermal parameters were obtained by theoretical calculation (C–H = 0.96 Å). The final R factors were $R = 0.0529$ and $R_w = 0.0562$ with 1385 reflections. The atomic fractional coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms, and isotropic thermal parameters of the hydrogen atoms are given in Table 3 and 4, respectively. The bond lengths and selected bond angles are listed in Table 5.

Results and discussion

*Preparation of complexes **4–10***

Compound **1** was treated with a *ca.* 10% molar excess of aryllithium, ArLi (Ar = C_6H_5, *o*-,*m*-,*p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$) in diethyl ether at -70–45°C for 3–4 h, and the acylmetalate intermediates formed were subse-

Table 2

^{1}H NMR spectra of complexes **4–13** in acetone-d_6 at 20°C (δ ppm), TMS as internal reference

Complex	δ (cycloolefin-proton)	δ (aryl-proton)	δ (OCH_2CH_3)
4	4.40 (t, 4), 3.80 (m, 2) 1.35 (t, 2)	7.83 (m, 3), 6.63 (m, 2)	3.93 (q, 2), 1.22 (t, 3)
5	4.36 (t, 4), 3.65 (m, 2) 1.35 (t, 2)	7.14 (m, 4) 2.32 (s, 3)(*o*-$CH_3C_6H_4$)	3.70 (q, 2), 1.17 (t, 3)
6	4.38 (t, 4), 3.82 (m, 2) 1.30 (t, 2)	7.32 (m, 3), 6.45 (m, 1) 2.33 (s, 3)(*m*-$CH_3C_6H_4$)	3.92 (q, 2), 1.17 (t, 3)
7	4.36 (t, 4), 3.63 (m, 2) 1.35 (t, 2)	7.20 (m, 4) 2.40 (s, 3)(*p*-$CH_3C_6H_4$)	3.93 (q, 2), 1.15 (t, 3)
8	4.76 (t, 4), 3.74 (m, 2) 1.30 (t, 2)	7.18 (m, 4) 3.75 (s, 3)(*p*-$CH_3OC_6H_4$)	3.80 (q, 2), 1.12 (t, 3)
9	4.45 (t, 4), 3.70 (m, 2) 1.35 (t, 2)	7.70 (d, 2), 6.85 (d, 2)	4.01 (q, 2), 1.23 (t, 3)
10	4.76 (t, 4), 3.74 (m, 2) 1.32 (t, 2)	7.15 (m, 3), 6.66 (m, 1) 2.93 (s, 3)(*o*-$CH_3C_6H_4$)	3.86 (q, 2), 1.27 (t, 3)
11	4.62 (broad singlet, 4) 3.00 (b.s, 8)	7.25 (m, 5)	5.18 (q, 2), 1.78 (t, 3)
12	4.60 (broad singlet, 4) 2.64 (b.s, 8)	7.20 (m, 4) 2.33 (s, 3)(*o*-$CH_3C_6H_4$)	5.50 (q, 2), 1.29 (t, 3)
13	4.62 (broad singlet, 4) 2.65 (b.s, 8)	8.00 (d, 2), 7.08 (d, 2) 3.94 (s, 3)(*p*-$CH_3OC_6H_4$)	5.17 (q, 2), 1.74 (t, 3)

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (2×10^3)

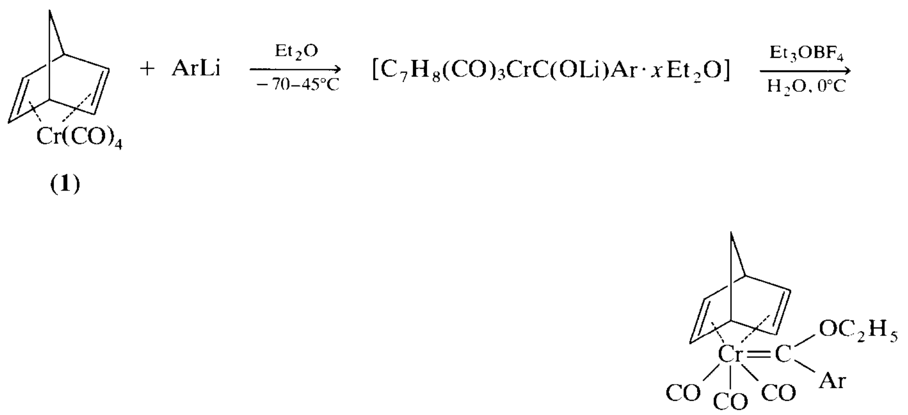
Atom	x	y	z	U [a]
Cr	8010(1)	6982(1)	3402(1)	25(1)
Co(1)	8097(8)	6264(6)	4602(5)	33(2)
Co(2)	7729(7)	7825(5)	2284(5)	29(2)
Co(3)	7327(7)	8207(6)	4021(5)	33(2)
O	5767(5)	5777(4)	3999(4)	33(2)
C(1)	6248(7)	6448(5)	3328(6)	29(2)
C(2)	4405(7)	5469(7)	4065(6)	39(3)
C(3)	4274(7)	4741(7)	4898(5)	38(2)
C(4)	5259(6)	6827(6)	2613(5)	25(2)
C(5)	4587(7)	7807(6)	2738(5)	30(2)
C(6)	3761(7)	8197(6)	2024(5)	33(2)
C(7)	3588(7)	7626(6)	1201(5)	27(2)
C(8)	4252(8)	6651(6)	1068(6)	38(3)
C(9)	5081(7)	6246(6)	1774(5)	32(2)
C(10)	2708(7)	8058(7)	438(5)	37(2)
O(1)	8132(6)	5906(5)	5345(4)	46(2)
O(2)	7589(5)	8393(4)	1651(4)	41(2)
O(3)	6808(6)	8952(5)	4364(4)	46(2)
C(21)	10113(6)	7041(7)	3806(5)	31(2)
C(22)	10458(7)	5828(6)	3537(5)	32(2)
C(23)	9199(7)	5416(6)	3088(5)	31(2)
C(24)	9018(7)	5973(6)	2244(5)	33(2)
C(25)	10209(7)	6760(6)	2154(6)	39(3)
C(26)	9947(7)	7604(6)	2942(5)	35(2)
C(27)	11255(8)	6032(7)	2618(6)	40(3)

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

quently alkylated with Et_3OBF_4 in aqueous solution at 0°C. After removal of the solvent in a high vacuum at low temperature, the solid residue was chromatographed on an alumina column at −20°C, and the crude product was recrystallized from petroleum ether/CH_2Cl_2 or petroleum ether/ether solution at −80°C to give orange-red norbornadiene-coordinated carbene complexes $C_7H_8(CO)_3CrC(OC_2H_5)Ar$ (**4–9**) in 44–61% yields (eq. 3). However, when C_6Cl_5Li was used as nucleophile for the reaction with **1** under the same conditions, no analogous complex was obtained. This may be due to the electron-withdrawing effect and the steric hindrance of the chlorine atoms.

Unexpectedly, the tungsten compound **2** reacted with aryllithium reagents under the same conditions only in the case of *o*-$CH_3C_6H_4Li$. The acylmetalate formed was alkylated with Et_3OBF_4 to give the analogous orange-red crystalline complex $C_7H_8(CO)_3WC(OC_2H_5)C_6H_4CH_3$-*o* (**10**) in 62% yield (eq. 4). However, C_6H_5Li, *m*-,*p*-$CH_3C_6H_4Li$, *p*-$CH_3OC_6H_4Li$, and *p*-$CF_3C_6H_4Li$ gave no analogous products owing to the rapid decomposition of the acylmetalate intermediates formed during the alkylation with Et_3OBF_4 in aqueous solution or in CH_2Cl_2 solution.

Complexes **4–9** and **10** are formulated as norbornadiene(tricarbonyl)[ethoxy(aryl)carbene]-chromium and -tungsten complexes, respectively, based on their IR, ^1H NMR and mass spectra, and elemental analyses. Product **7** was established by an X-ray crystallographic study (see below) to have a structure in which the added ethoxy and aryl groups are at the carbene carbon atom, and the metal atom is coordinated to the diene portion of the norbornadiene ligand. The IR spectrum and the solution ^1H NMR spectrum are consistent with this structure.



(3)

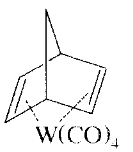
4: Ar = C_6H_5
5: Ar = *o*-$CH_3C_6H_4$
6: Ar = *m*-$CH_3C_6H_4$
7: Ar = *p*-$CH_3C_6H_4$
8: Ar = *p*-$CH_3OC_6H_4$
9: Ar = *p*-$CF_3C_6H_4$

Table 4

Hydrogen coordinates ($\times 10^4$) and isotropic thermal parameters (2×10^3) for 7

Atom	x	y	z	U [a]
H(2a)	3884	6119	4146	45
H(2b)	4139	5085	3505	45
H(3a)	3394	4514	4978	43
H(3b)	4553	5136	5450	43
H(3c)	4808	4102	4808	43
H(5)	4539	8341	3239	38
H(6)	3416	8872	2277	37
H(8)	3990	6401	454	48
H(9)	5425	5572	1521	39
H(10a)	2308	8738	629	43
H(10b)	2055	7515	313	43
H(10c)	3208	8181	−123	43
H(21)	10611	7288	4316	42
H(22)	10826	5378	4026	37
H(23)	9094	4637	3194	37
H(24)	8764	5665	1647	37
H(25)	10393	7071	1544	48
H(26)	10281	8314	2764	42
H(27a)	11421	5369	2266	46
H(27b)	12053	6413	2732	46

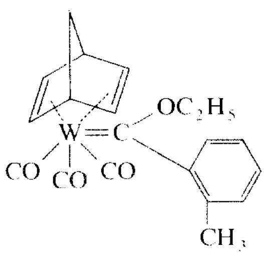
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.



(2)

$+ \ o\text{-}CH_3C_6H_4Li \xrightarrow[-60 \sim -50^\circ C]{Et_2O}$

$[C_7H_8(CO)_3WC(OLi)C_6H_4CH_3 \cdot xEt_2O] \xrightarrow[H_2O,\ 0^\circ C]{Et_3OBF_4}$ (4)



(10)

Complexes **4–10** were all soluble both in polar and non-polar organic solvents. They were sensitive to air and temperature, and decomposed partially on exposure to air even in the solid state. Complex **9** was extremely sensitive to air and burned rapidly on exposure to air. The IR spectra (Table 1) of complexes **4–10** showed three strong CO absorption bands in the ν(CO) region which indicated that an $M(CO)_3$ (M = Cr or W) moiety exists in these complexes. In the ^{1}H NMR spectra (Table 2), the chemical shift, multiplicity and integral intensity of the proton signals attributed to the norbornadiene ligand are essentially the same as those of starting material **1**, which suggests that the added ethoxy and aryl substituent exert

Table 5

Bond lengths (Å) and selected bond angles (deg) for **7**

Cr–Co(1)	1.909(8)	Cr–Co(2)	1.905(7)	Cr–Co(3)	1.861(8)
Cr–C(1)	1.942(7)	Cr–C(21)	2.255(6)	Cr–C(23)	2.302(7)
Cr–C(24)	2.295(8)	Cr–C(26)	2.241(8)	Co(1)–O(1)	1.139(9)
Co(2)–O(2)	1.138(9)	Co(3)–O(3)	1.157(9)	O–C(1)	1.344(9)
O–C(2)	1.464(9)	C(1)–C(4)	1.512(10)	C(2)–C(3)	1.478(12)
C(4)–C(5)	1.387(10)	C(4)–C(9)	1.392(10)	C(5)–C(6)	1.407(10)
C(6)–C(7)	1.366(10)	C(7)–C(8)	1.378(11)	C(7)–C(10)	1.507(10)
C(8)–C(9)	1.405(11)	C(21)–C(22)	1.557(11)	C(21)–C(26)	1.409(11)
C(22)–C(23)	1.535(11)	C(22)–C(27)	1.561(11)	C(23)–C(24)	1.384(10)
C(24)–C(25)	1.565(11)	C(25)–C(26)	1.536(11)	C(25)–C(27)	1.544(11)
Co(1)–Cr–Co(2)	171.7(3)	Co(1)–Cr–Co(3)	87.8(3)	Co(2)–Cr–Co(3)	84.6(3)
Co(1)–Cr–C(1)	86.8(3)	Co(2)–Cr–C(1)	89.4(3)	Co(3)–Cr–C(1)	86.1(3)
Co(1)–Cr–C(21)	75.1(3)	Co(2)–Cr–C(21)	110.0(3)	Co(3)–Cr–C(21)	102.9(3)
C(1)–Cr–C(21)	159.1(3)	Co(1)–Cr–C(23)	76.8(3)	Co(2)–Cr–C(23)	111.2(3)
Co(3)–Cr–C(23)	161.7(3)	C(1)–Cr–C(23)	102.7(3)	C(21)–Cr–C(23)	63.7(3)
Co(1)–Cr–C(24)	111.8(3)	Co(2)–Cr–C(24)	76.2(3)	Co(3)–Cr–C(24)	158.9(3)
C(1)–Cr–C(24)	102.3(3)	C(21)–Cr–C(24)	76.0(3)	C(23)–Cr–C(24)	35.0(3)
Co(1)–Cr–C(26)	111.6(3)	Co(2)–Cr–C(26)	73.5(3)	Co(3)–Cr–C(26)	102.2(3)
C(1)–Cr–C(26)	160.0(3)	C(21)–Cr–C(26)	36.5(3)	C(23)–Cr–C(26)	74.9(3)
C(24)–Cr–C(26)	64.1(3)	Cr–Co(1)–O(1)	175.1(7)	Cr–Co(2)–O(2)	175.1(6)
Cr–Co(3)–O(3)	174.2(7)	C(1)–O–C(2)	123.8(7)	Cr–C(1)–O	120.8(5)
Cr–C(1)–C(4)	125.0(5)	O–C(1)–C(4)	113.9(6)	O–C(2)–C(3)	107.0(6)
C(1)–C(4)–C(5)	121.0(6)	C(1)–C(4)–C(9)	120.6(6)	Cr–C(21)–C(22)	97.5(4)
Cr–C(21)–C(26)	71.2(4)	C(22)–C(21)–C(26)	105.7(6)	C(21)–C(22)–C(23)	102.2(5)
C(21)–C(22)–C(27)	100.1(6)	C(23)–C(22)–C(27)	99.1(6)	Cr–C(23)–C(24)	72.2(4)
C(22)–C(23)–C(24)	108.3(6)	Cr–C(24)–C(23)	72.8(4)	Cr–C(24)–C(25)	95.4(4)
C(23)–C(24)–C(25)	105.0(6)	C(24)–C(25)–C(26)	101.8(6)	C(24)–C(25)–C(27)	100.0(6)
C(26)–C(25)–C(27)	101.2(6)	Cr–C(26)–C(21)	72.3(4)	Cr–C(26)–C(25)	98.4(5)
C(21)–C(26)–C(25)	106.8(6)	C(22)–C(27)–C(25)	94.1(6)	Cr–C(23)–C(22)	96.2(4)

no significant influence on the proton signals of the cyclodiene ligand. In addition, in contrast to complexes $C_7H_8(CO)_2MoC(OC_2H_5)Ar$ and $C_7H_8(CO)_3MoC(OC_2H_5)Ar$ [11], in the solution ^1H NMR spectra, no *cis–trans* geometrical isomers arising from the difference in the steric arrangement of the ethyl and aryl group with regard to the $C_{carbene}$–O partial double band were observed, perhaps owing to rapid *cis–trans* isomerization. The characteristic mass spectral peaks (m/z) of complexes **4–10** are given in the Experimental section. All of these complexes showed their molecular ions and the principal fragmentations produced by successive loss of CO ligand. In addition, the ion peaks of $m(CO)_3^+$, $m(CO)_2^+$, $m(CO)^+$, and m^+ (m = Cr or W) are seen, which further corroborated that a $M(CO)_3$ moiety exists in the molecules of complexes **4–10**.

Structure of $C_7H_8(CO)_3CrC(OC_2H_5)C_6H_4CH_3$-p (7)

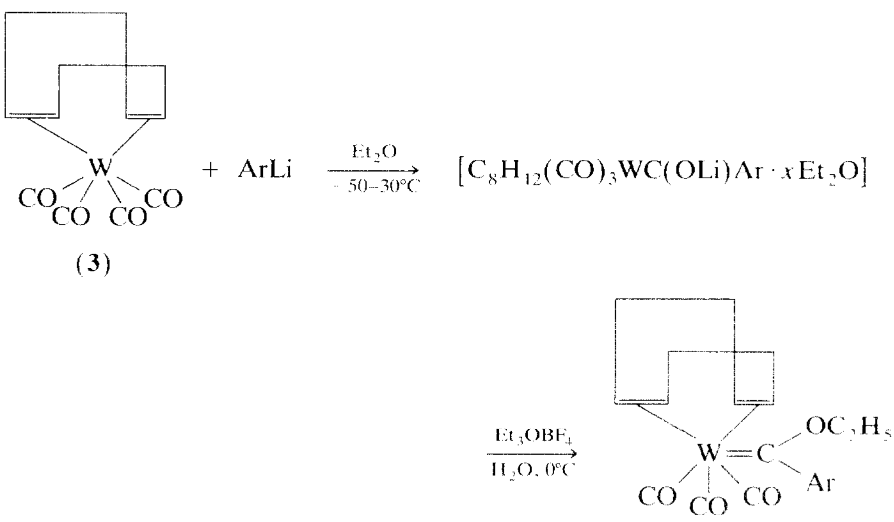
The structure illustrated in Fig. 1 is generally similar to that of the molybdenum complex $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4CH_3$-*p* [11]. In complex **7**, the central Cr atom coordinated to C(1), Co(1), Co(2), Co(3), C(21), C(23), C(24), and C(26) constructs an eight-coordinating distorted square bipyramid and satisfies the 18-electron rule.

The Cr–C(CO) distances of 1.909(8), 1.905(7) and 1.861(8) Å are slightly shorter than that of the Cr–C(1)$_{carbene}$ bond (1.942(7) Å. Also the bond lengths of Cr–C(CO) and Cr–C(1)$_{carbene}$ are shorter than that of Mo–C(CO) (1.99–2.07 Å) and Mo–C$_{carbene}$ (2.06(4) Å) in $C_7H_8(CO)_3MoC(OC_2H_5)C_6H_4CH_3$-*p*, which can probably be attributed to the difference in atomic radius of Cr and Mo. The four carbon atoms (C(21), C(23), C(24) and C(26)) of the norbornadiene ligand are π bonded to the Cr atom with bond lengths of 2.241–2.302 Å. In the cyclodiene ligand, the C(21)–C(26) distance of 1.409(11) Å and C(23)–C(24) distance of 1.384(10) Å are obviously shorter than the other C–C distances (1.535–1.565 Å), which indicated that both bonds have double bond character. In molecule **7**, the plane defined by Co(1)O(1)Co(2)O(2) is essentially perpendicular to that of Co(3)O(3)C(1). Moreover, the two planes lie well distributed in the four Cr–C coordinated bonds (Cr–C(21), Cr–C(23), Cr–C(24) and Cr–C(26)). The molecule now has a crisscross configuration, so that it has lower energy for a stable existence.

Preparation of complexes 11–13

The reaction analogous to that of norbornadiene(tetracarbonyl)chromium (**1**) and -tungsten (**2**) (eqs. 3 and 4) also occurs with (1,5-COD)W(CO)$_4$ (**3**). Thus, *ca.* 50% molar excess of aryllithium reagents reacted with **3** at −50–30°C during 3–4 h to afford three crystalline complexes with the compositions $C_8H_{12}(CO)_3WC(OC_2H_5)Ar$ (**11**: Ar = C_6H_5; **12**: Ar = *o*-$CH_3C_6H_4$; **13**, Ar = *p*-$CH_3OC_6H_4$) formulated as 1,5-cyclooctadiene(tricarbonyl)[ethoxy(aryl)carbene]-tungsten complexes in 28–32% yields (eq. 5).

The diamagnetic complexes **11–13** are soluble in polar and non-polar organic solvents. They are very sensitive to air and temperature, similar to the above norbornadiene coordinated chromium and tungsten carbene complexes. The struc-



(5)

11: Ar = C_6H_5
12: Ar = *o*-$CH_3C_6H_4$
13: Ar = *p*-$CH_3OC_6H_4$

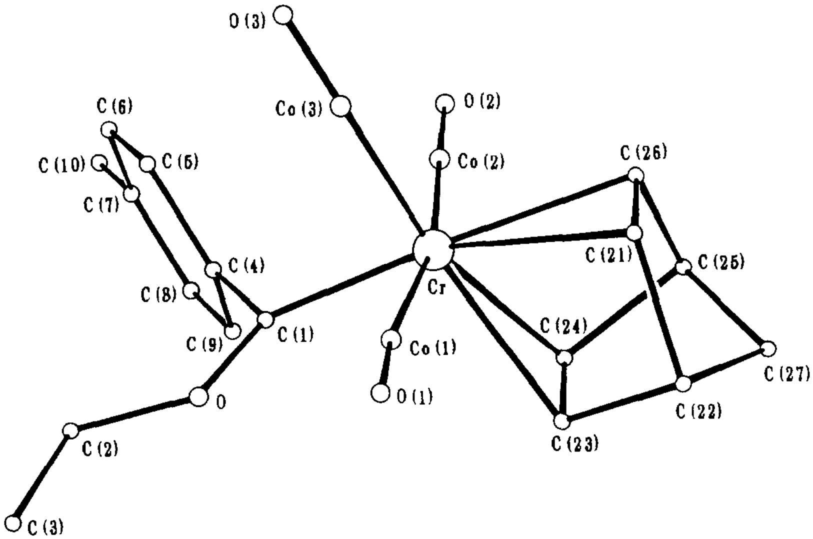


Fig. 1. Molecular structure of 7.

ture of complexes **11–13** was determined by IR (Table 1), ^{1}H NMR (Table 2) and mass spectra, and elemental analyses. In the ^{1}H NMR spectra of the complexes, the chemical shift, multiplicity and integral intensity of the proton signals attributed to the 1,5-COD ligand are essentially the same as that of **3**, which showed that no isomerization of the 1,5-COD ligand occurred during the reaction of **3** with aryllithium and the subsequent alkylation with Et_3OBF_4.

Conclusion

As mentioned in the Introduction, the reaction of the olefin-ligated metalcarbonyl compounds with aryllithium reagents and subsequent alkylation reaction produced normal or isomerized olefin-coordinated metal carbene complexes. The stability of the acylmetalate intermediates or products depends not only on the olefin ligand, but also on the central metal atoms. For example, in the case of the norbornadiene and 1,5-cyclooctadiene ligand, when the central metal is Fe, the isomerization of the cyclodiene ligand occurred during the reaction to give ring-opened diallyliron complexes [5] and (η^6-arene)-dicarbonyliron complexes [8], respectively. When the central metal is Cr, Mo [11], or W, no isomerization occurred during the reaction to afford the normal cyclodiene-coordinated carbene complexes in which the diene ligand and carbene ligand coexist stably. In general, the diene-coordinated carbene complexes of the Group VIB metals (d^6) are more stable than those of the Group VIIIB metals (d^8), which may be due to the difference in their outer shell electronic configuration.

With regard to the Group VIB metals (Cr, Mo, and W), the norbornadiene-coordinated carbonyl compounds of Cr and Mo reacted with most aryllithium reagents (such as C_6H_5Li, *o-,m-,p*-$CH_3C_6H_4Li$, *p*-$CH_3OC_6H_4Li$ and *p*-$CF_3C_6H_4Li$), followed by alkylation with Et_3OBF_4 to give the norbornadiene-coordinated carbene complexes of Cr and Mo [11], respectively. However, the norbornadiene-coordinated tungsten compound (**2**) reacted only with o-$CH_3C_6H_4Li$ to give the analogous carbene complex. Similar results were observed in the case of the cycloheptatriene ligand. Cycloheptatriene(tricarbonyl)molybdenum treated with aryllithium reagents followed by alkylation with Et_3OBF_4 gave the cycloheptatriene-coordinated carbene complexes [11], while the chromium and tungsten compounds reacted similarly with aryllithium to afford 7-exo-(lithiumcycloheptatriene)tricarbonyl-chromium and -tungsten. After treatment with CH_3I, the 7-exo-(methylcycloheptatriene)tricarbonyl-chromium and -tungsten [20] were obtained, respectively.

On the other hand, for the identical central metal but different olefin-ligated metal carbonyls, the reactivities with aryllithium reagents are different. For instance, the reaction of 1,5-cyclooctadiene(tetracarbonyl)tungsten with aryllithium such as C_6H_5Li, o-$CH_3C_6H_4Li$, and p-$CH_3OC_6H_4Li$, and subsequent alkylation with Et_3OBF_4 gave the 1,5-COD-coordinated carbene complexes, while norbornadiene compound (**2**) reacted similarly only in the case of o-$CH_3C_6H_4Li$. In contrast, C_6H_5Li and p-$CH_3OC_6H_4Li$ gave no analogous carbene complexes but decomposition reactions occurred.

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