Journal of Organometallic Chemistry, 376 (1989) 353–358
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20145

$\{\eta^6$-1,4-$(CH_3SO_3)_2C_6H_4\}Cr(CO)_3$: synthesis, characterization, and reactivity

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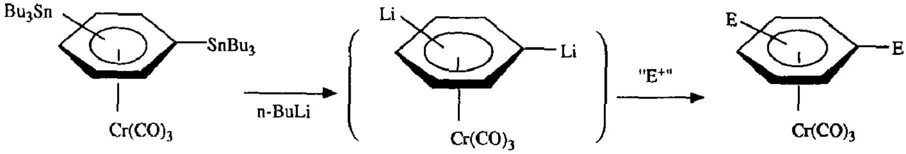
(Received May 1st, 1989)

Abstract

Reaction of $(MeCN)_3Cr(CO)_3$ with hydroquinone in refluxing tetrahydrofuran (THF) produced $\{\eta^6$-1,4-$C_6H_4(OH)_2\}Cr(CO)_3$ (**1**) which was subsequently converted to $\{\eta^6$-1,4-$(CH_3SO_3)_2C_6H_4\}Cr(CO)_3$ (**2**) by treatment with methanesulfonyl chloride and triethylamine. A single-crystal X-ray study of **2** has been completed and is reported. Treatment of **2** with an oxygen nucleophile gave reaction at sulfur; whereas, treatment of **2** with lithium phenylacetylide resulted in decomposition of the complex to metallic chromium.

Although (η^6-arene)$Cr(CO)_3$ complexes were discovered over three decades ago [1], still today they are producing new and exciting advancements in the areas of synthetic reagents [2], pharmaceutical chemistry [3], and as models for electron-transfer processes [4]. Our current interest in (η^6-arene)$Cr(CO)_3$ complexes involves their incorporation into conjugated organic polymer backbones via palladium-catalyzed polycondensation reactions [5]. The latter reaction requires bis-functionalized (η^6-arene)$Cr(CO)_3$ complexes and stimulated our recent synthesis of such complexes (eq. 1) [6]. In this paper we wish to present an efficient synthesis of the title compound and its characterization and reactivity towards nucleophiles.



(1)

The strategy for the synthesis of **2** involves complexing an "electron rich" arene (i.e. hydroquinone) to the $Cr(CO)_3$ unit and then modifying the hydroxy groups to more desirable and reactive functional groups (eq. 2). Although $\{\eta^6$-$C_6H_5OH\}Cr(CO)_3$ [7a] and other hydroxy-substituted (η^6-arene)$Cr(CO)_3$ [7b] complexes have been reported, this is the first successful preparation of a dihydroxyarene-$Cr(CO)_3$

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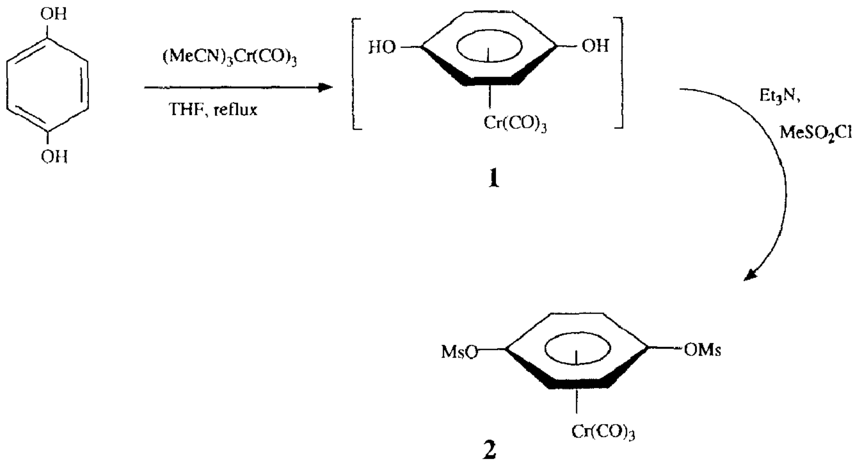

(2)

complex [7c*]. A crucial factor in the synthesis of **1** was the use of THF. Other higher boiling solvents such as *p*-dioxane led to decomposition of **1** as it was formed in the reaction. Complex **1** was isolated in crude form and characterized spectroscopically. Extensive efforts were not made to purify the complex in part because of its air- and heat-sensitivity, but rather, it was found to be most efficient to convert the complex to a more desirable system.

Complex **1** was treated with triethylamine and then methanesulfonyl chloride. The conversion of **1** (ν(C≡O) 1960 and 1876 cm^{-1}) to **2** (ν(C≡O) 1992 and 1924 cm^{-1}) could be easily monitored by infrared spectroscopy because of the significant change for the carbonyl bands. New bands at 1923 and 1863 cm^{-1} did appear in the infrared spectrum after the addition of the triethylamine prior to the addition of the methanesulfonyl chloride. These new bands are likely the result of **1** undergoing mono-deprotonation. Complex **2** was purified by recrystallization ($CHCl_3$, 60 to −25 °C) to afford air-stable yellow crystals.

Complex **2** has been characterized by a single-crystal X-ray diffraction study. A drawing of crystalline **2** is presented in Fig. 1 along with selected bond lengths. Complex **2** appears to have normal bond lengths and angles similar to crystal structures of related $\{\eta^6\text{-arene}\}Cr(CO)_3$ compounds [8].

We have studied the reactivity of **2** towards carbon and oxygen nucleophiles (Scheme 1) [9*]. Treatment of **2** with excess potassium (−)-myrtanoxide for 15 min at ambient temperature followed by addition of methyl iodide produced complexes **3** [10] and **4** (product ratio 5/1, respectively). The isolation of **4** would suggest that the displacement was likely step-wise in nature.

Reaction of **2** with lithium phenylacetylide in ether at −78 °C resulted in complete destruction of **2** and the formation of pyrophoric chromium. Complex **5** was prepared by an alternative route to demonstrate that indeed the target molecule was stable and isolable. The Stille reaction [11*] afforded **5** in good yield (84%)

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* Reference number with asterisk indicates a note in the list of references.

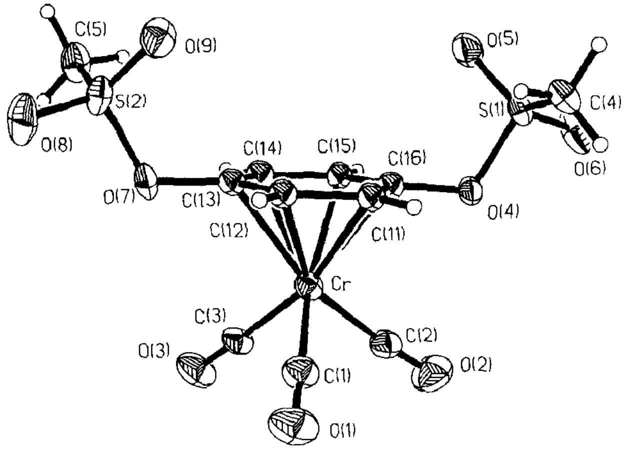
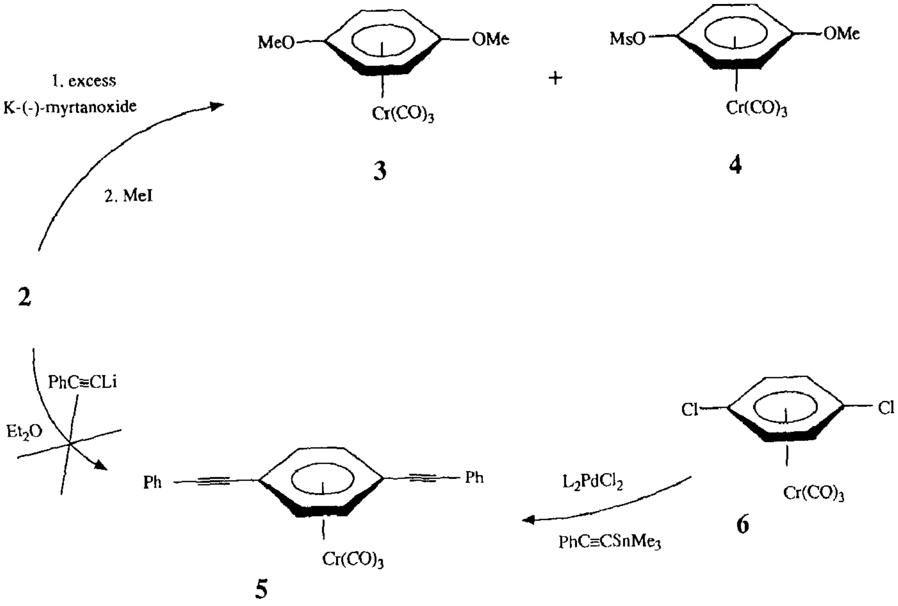


Fig. 1. Drawing of crystalline **2** including the labeling scheme. Hydrogen atoms have been drawn with arbitrarily small thermal coefficients for clarity. Selected bond distances (Å) Cr–C(11), 2.204(2); Cr–C(1), 1.874(8); S(1)–C(4), 1.722(8), S(1)–O(4), 1.617(5); S(1)–O(5), 1.409(7); C(11)–C(16), 1.398(1); C(11)–C(12), 1.439(1); C(12)–C(13), 1.378(1); C(13)–C(14), 1.415(1); C(14)–C(15), 1.420(1), C(15)–C(16), 1.393(1).

from the palladium-catalyzed cross-coupling of trimethyl(phenylethynyl)stannane and complex **6** [6].

The results of this study demonstrate the feasibility of preparing the (η^6-hydroquinone)$Cr(CO)_3$ complex and that it can serve as a precursor to other functionalized complexes. Further work in our laboratory will focus on the synthesis of other aryl- and perfluoroalkylsulfonate esters to develop more reactive and perhaps useful intermediates.



Scheme 1

Experimental

General. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents [12]. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ vs. Me_4Si in ^{1}H NMR and assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. The $(PPh_3)_2PdCl_2$ [13], (trimethylstannylethynyl)benzene [14], and (η^6-1,4-dichlorobenzene)$Cr(CO)_3$ [6] were prepared by literature methods. The hydroquinone, (−)-myrtanol, trimethylchlorostannane, and phenyl acetylene were purchased from Aldrich Chemical Company and used as received. The chromium hexacarbonyl was purchased from Pressure Chemical Company. The palladium(II) chloride was purchased from Alfa. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, Georgia.

Preparation of {η^6-1,4-bis$(CH_3SO_3)C_6H_4$}$Cr(CO)_3$ *(2).* A THF (60 ml) solution containing $(CH_3CN)_3Cr(CO)_3$ (prepared from 3.00 g (13.6 mmol) of $Cr(CO)_6$ heated at reflux for 24 h in acetonitrile/THF, 50/5 ml, followed by solvent removal under reduced pressure) was treated with *p*-hydroquinone (1.65 g, 15.0 mmol) and then heated at reflux for 72 h. A sample from the reaction mixture was taken and the solvent removed under reduced pressure to afford a yellow solid. Spectroscopic data for crude **1**: ^{1}H NMR ($CDCl_3$) δ 5.20 (s, arene CH's); ^{13}C NMR ($CDCl_3$) δ 234.8 (CO), 133.5 (*ipso*-arene carbon), 81.7 (arene *C*H); IR (CH_2Cl_2) ν(C≡O) 1960 (s, sharp) and 1876 (vs, broad) cm^{-1}. The reaction mixture was treated with triethylamine (7.8 ml, 54 mmol) and cooled to 0 °C before methanesulfonyl chloride (30 mmol) was added in a drop-wise manner. After the addition was complete the mixture was stirred for an additional 30 min and then diluted with chloroform (150 ml). The mixture was washed with water (2 × 150 ml) and then dried over potassium carbonate. The solvents were removed under reduced pressure and the product recrystallized from chloroform to afford analytically pure **2** (1.10 g, 20%): ^{1}H NMR ($CDCl_3$) δ 5.51 (s, 4H), 3.15 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 229.2 (CO), 124.8 (*ipso*-carbon), 84.8 (CH arene), 38.4 (CH_3); IR (CH_2Cl_2) ν(C≡O) 1992 (s, sharp) and 1924 (vs, broad) cm^{-1}. Anal. Found: C, 32.93; H, 2.58. $C_{11}H_{10}CrO_9S_2$ calcd.: C, 32.84; H, 2.51%.

Reaction of **2** *with potassium (−)-myrtanoxide.* A THF (10 ml) solution containing **2** (0.20 g, 0.5 mmol) was treated with a THF solution of potassium myrtanoxide (ca. 6 equiv.) for 15 min at ambient temperature. The mixture was then treated with excess methyl iodide (ca. 10 equiv.) and diluted with chloroform. The organic layer was washed with water (2 × 100 ml) and dried over potassium carbonate. The solvents were removed under reduced pressure and crude product subjected to column chromatography (10% ethyl acetate/hexanes to 50% ethyl acetate/hexanes). The first yellow band off the column was identified as **3** followed by a second yellow band which gave spectroscopic data consistent with the structure of **4**: ^{1}H NMR ($CDCl_3$) δ 5.75 (d, *J* 7.1 Hz, 2H), 5.10 (d, *J* 7.1 Hz, 2H), 3.67 (s, 3H), 3.22 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 231.2 (CO), 88.5, 76.5 (CH arene), 56.2 (OCH_3), 38.1 (OSO_2CH_3); IR (CH_2Cl_2) ν(C≡O) 1977 (s, sharp) and 1902 (vs, broad) cm^{-1}.

Preparation of **5**. A dichloromethane (5 ml) solution containing (η^6-1,4-dichlorobenzene)$Cr(CO)_3$ (0.13 g, 0.46 mmol), (trimethylstannylethynyl)benzene (0.60 g, 2.3 mmol), and $(PPh_3)_2PdCl_2$ (13 mg, 2 mol%) was prepared and allowed to react for 72 h at ambient temperature. The mixture was diluted with dichloromethane (20 ml), washed with water (2 × 25 ml), and the organic layer dried over potassium carbonate. The solvent was removed and product recrystallized by diffusion of ether into a dichloromethane solution of **5** (0.15 g, 84%). ^1H NMR ($CDCl_3$): 7.55 (m, 2 H), 7.38–7.34 (m, 3 H), 5.58 (s, 2 H); ^{13}C NMR ($CDCl_3$); 231.6 (C≡O), 131.9, 129.1, 128.4 (arene CH's), 121.7 (arene C), 93.8 (η^6-arene CH's), 90.2, 88.7, 85.0 (η^6-arene C and alkyne C's); IR (CH_2Cl_2): ν(C≡O) 1976 (s, sharp) and 1911 (vs, broad) cm^{-1}. Anal. Found: C, 70.72; H, 3.60. $C_{23}H_{14}CrO_3$ calcd.: C, 70.77; H, 3.61%.

X-ray diffraction study of **2**. Yellow needles of **2** (0.06 × 0.08 × 0.40 mm) suitable for X-ray analysis were grown from a $CHCl_3$ solution at −25 °C over a period of several days. Crystallographic data: $C_{11}H_{10}CrO_9S_2$, cryst. size 0.06 × 0.08 × 0.40 mm, triclinic, $P1$, a 8.059(2), b 9.173(4), c 11.780(5) Å, α 112.23 (3), β 101.28 (3), γ 93.42° (2), V 781.9(5) $Å^3$, $Z = 2$, D_{calcd} 1.709 g cm^{-3}, μ(Mo-K_α) 10.1 cm^{-1}, T 20 °C. Intensity data (2θ–θ, $3° < \theta < 50°$, variable scan speed of 3.0–1.50 °/min, 2759 independent reflections, 1734 with $F_o > 3.0\sigma(F_o)$) were collected on a Nicolet R3m/V diffractometer and the structure initially solved by Patterson and then completed using difference Fourier syntheses (Nicolet SHELXTL PLUS program package). The carbons in the six-membered ring were refined using isotropic thermal parameters and as a rigid rotor (to increase the N_o/N_v ratio). The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the structure and refined having an idealized bond length (C–H 0.96 Å) and isotropic thermal parameters, R_F 6.64%, R_{wF} 6.16%, GOF = 1.37, $\Delta/\sigma = 0.002$, largest peak in the final difference map was 0.50 e $Å^{-3}$, $N_o/N_v = 10.8$.

Supplementary material available. A listing of final atomic positions, anisotropic thermal parameters, bond lengths and angles, and a listing of structure factors for the single-crystal X-ray diffraction study of **2** (15 pages). ordering information can be obtained from the authors.

Acknowledgment

MEW is indebted to Prof. John L. Hubbard for solving the X-ray structure of **2** and providing the crystallographic data. MEW also wishes to thank Prof. Tom G. Richmond for sharing results from his laboratory prior to publication. The author wishes to thank Petroleum Research Fund administered by the American Chemical Society for partial funding of this research.

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