Organometallics **1989**, *8*, 461-467

Chemistry of (η-Phenoxide)Cr(CO)$_3$ Ligands

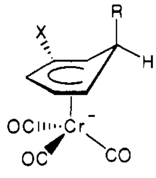
Joseph A. Heppert,* Timothy J. Boyle, and Fusao Takusagawa

Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045

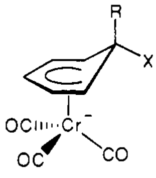
Received June 29, 1988

(η^6-Phenol)tricarbonylchromium complexes are conveniently converted to $[(\eta^6\text{-phenoxide})Cr(CO)_3]^-$ species on treatment with aqueous base. The phenoxide chromium anions, which are readily isolated as crystalline tetraethylammonium salts, react with main-group electrophiles ((p-tol)SO_2Cl or CF_3COCl) to produce new sulfonate- and carboxylate-substituted arene chromium complexes. Similar reactions between the phenoxide anions and metal electrophiles ($CpFe(CO)_3^+$ or Cp_2ZrCl_2) result in electron-transfer reactions that consume the starting arene complexes. Transition-metal complexes bearing (η-phenoxide)Cr(CO)$_3$ ligands are conveniently prepared through alcoholysis reactions with metal alkoxide and metal dimethylamide precursors. An X-ray crystallographic study of $Cp_2Zr\{(\eta\text{-}OC_6H_5)Cr(CO)_3\}_2$ was carried out. For 1403 unique intensity data collected by using Cu Kα radiation in a θ–2θ scan procedure, the space group for the molecule was determined to be *Pnma* with unit cell parameters a = 15.023 (3) Å, b = 21.864 (5) Å, and c = 8.073 (2) Å. The refinement converged to an $R(F)$ of 0.078 and an $R_w(F)$ of 0.089. The molecule shows general structural features common to other bent zirconocene and π-arene chromium complexes but shows some unexpected features associated with the Zr–aryloxide bonding. Little evidence is found for either steric interactions between the (η-OC_6H_5)Cr(CO)$_3$ units or for Zr–O π bonding. The O–arene bond does show a small degree of multiple-bond character. This observation is supported by the deviation of the O–C arene vector from the least-squares arene plane, suggesting that a small degree of a cyclohexadienone resonance form is contributing to Zr–arene bonding.

The widespread investigation of (η-arene)Cr(CO)$_3$ reagents for synthesis has been motivated by the radically new modes of reactivity observed at complexed arene ligands.[1] Among the most striking of the observed changes is the increased electrophilicity of arene carbon centers.[2] Nucleophiles with pK_A > 20 attack arene chromium complexes to produce stable Meisenheimer-like complexes (1).[1a] These cyclohexadienide intermediates show a remarkable degree of flexibility in subsequent functionalization reactions, being readily transformed into 1,3-cyclohexadiene, cyclohexadienone, or simple substituted aromatic molecules.[1b] An important characteristic of some halide-substituted η^5-cyclohexadienide intermediates (2) is their ability to rearrange to a gem-disubstituted isomer, which subsequently decomposes through loss of the halide ion.[1c] These reactions have resulted in the transformation of a variety of arene C–F and C–Cl bonds into new C–C and C–X bonds (X = OR, SR).[1a-c]



1



2

In another recent development in arene chemistry, substituted aryloxide ligands have found a variety of applications in the synthesis of novel coordination compounds of the early transition metals.[3] Bulky 2,6-dialkylphenoxide ligands have been used to support mononuclear mixed alkyl/alkoxide complexes of Mo, Ta, Ti, and Zr.[4,5] Complexes of this type have been used to study the thermal and photoinduced activation of C–H bonds at d^0 metal centers.[3] Furthermore, the increased stability of S–C bonds in thioaryloxide ligands over those in simple thioalkoxide ligands has made bulky thioaryloxides a favored sulfur-containing ligand for early-transition-metal complexes.[5,6]

By contrast with these two important applications of arene ligands to transition-metal chemistry, it is surprising that few simple organic and organometallic compounds bearing (η-aryloxide)Cr(CO)$_3$ functional groups have been systematically investigated. One can postulate numerous novel applications for such molecules. For example, if traditionally poor leaving groups such as fluoride and chloride substituents are activated toward nucleophilic displacement in η-arene chromium complexes, will arene chromium complexes bearing activated oxygen leaving groups be suitable substrates for the conversion of arene C–O bonds into C–C bonds? Alternatively, will the added steric bulk of the Cr(CO)$_3$ pendent group help to stabilize some early-transition-metal aryloxide complexes without resorting to blocking the ortho arene sites with alkyl groups? We report herein the first systematic studies of the synthesis and reactivity of several new classes of (η-phenoxide)Cr(CO)$_3$ complexes.

Experimental Section

All reactions were carried out under a prepurified nitrogen atmosphere, using standard Schlenk techniques unless otherwise stated. Solvents were dried by conventional methods and freshly

---

(1) (a) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (b) Uemura, M.; Take, K.; Isobe, K.; Minami, T.; Hayashi, Y. *Tetrahedron* **1985**, *41*, 5771. (c) Kundig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (d) Rose-Munch, R.; Rose, E.; Semra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1551. (e) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901.

(2) (a) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957. (b) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091. (c) Semmelhack, M. F.; Hall, H. T. *Ibid.* **1974**, *96*, 7092. (d) Semmelhack, M. F.; Clark, G. *Ibid.* **1977**, *99*, 1675. (e) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Seaman, M. *Ibid.* **1979**, *101*, 217. (f) Semmelhack, M. F.; Yamashita, A. *Ibid.* **1980**, *102*, 5925. (g) Kundig, E. P.; Simmons, D. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1320. (h) Kundig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6967.

(3) Rothwell, I. P. *Polyhedron* **1985**, *4*, 179.

(4) For representative examples of publications covering these topics see: (a) Rothwell, I. P.; Latesky, S. L.; McMullen, A. K.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (b) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Ibid.* **1987**, *109*, 4270. (c) Rothwell, I. P.; Kerchner, J. L.; Fanwick, P. E. *Ibid.* **1987**, *109*, 5841. (d) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 1643. (e) Fanwick, P.; Oglivy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73. (f) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (g) Rothwell, J. P.; Chamberlain, L. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203.

(5) Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5924.

(6) (a) Dilworth, J. R.; Blower, P. J.; Zubietta, J. A. *Inorg. Chem.* **1985**, *24*, 2866. (b) Dilworth, J. R.; Bishop, P. T.; Zubietta, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 257.

0276-7333/89/2308-0461$01.50/0

distilled under nitrogen. NMR solvents were dried over 5-Å molecular sieves and degassed with a dry N_2 purge prior to use. ^1H and ^{13}C NMR spectra were obtained on a Varian XL 300-MHz spectrometer. ^1H NMR spectra were referenced against the residual proton impurity in benzene-d_6 or acetone-d_6, while ^{13}C NMR spectra were referenced against the resonances representing the aromatic carbons of benzene-d_6 or the methyl-group carbons of acetone-d_6. Infrared spectra were obtained on an IR/30 IBM FT instrument, using KBr pellet samples. Mass spectra were obtained on a Ribermag MS10, using a direct insert source. Elemental analyses were performed by Dersert Analytics, P.O. Box 41838, Tucson, AZ 85717. Phenol (Merck), 2,6-dimethylphenyl (Aldrich), 2,4,6-trimethylphenol (Aldrich), tetraethylammonium hydroxide (Aldrich), and hexacarbonyl chromium (Pressure Chemical) were used as received. $Cp_2Zr(NMe_2)_2$ was prepared according to the published procedure.[7a]

[η-(HO)C_6H_5]Cr(CO)$_3$. (Phenol)tricarbonylchromium was prepared by the following modification of the literature procedure.[7b] In an Erlenmeyer flask fitted with a nitrogen adapter, phenol (2.1 g, 22.7 mmol) was dissolved in dioxane (250 mL) and left to dry for 2 h over 5-Å molecular sieves. The dried solution was added to a Schlenk flask containing chromium hexacarbonyl (5 g, 22.7 mmol). This mixture was stirred and refluxed for 3 days. The solution was allowed to cool to room temperature and then filtered to remove any crystallized $Cr(CO)_6$. The filtrate was pumped dry, transferred to a water-cooled sublimator evacuated to 10^{-5} Torr, and warmed to 30 °C for 2 h. Free phenol and chromium hexacarbonyl collected on the cold finger. The yellow solid residue was recrystallized from a saturated toluene solution at −20 °C. Yield: 2.2–4.4 g (43–85%). ^1H NMR (acetone-d_6, 20 °C): δ 5.81 (2 H, t, *m*-Ar, J = 7.2 Hz), 5.32 (2 H, d, *o*-Ar, J = 6.3 Hz), 5.04 (1 H, t, *m*-Ar, J = 7.2 Hz). A large singlet at δ 3.58 may be due to a coordinated dioxane molecule which could not be eliminated from the sample. IR (cm^{-1}, CO stretching region): 1948, 1859.

[η-2,6-Me$_2$-1-(HO)C_6H_3]Cr(CO)$_3$ and [η-2,4,6-Me$_3$-1-(HO)C_6H_2]Cr(CO)$_3$. (2,6-Dimethylphenol)tricarbonylchromium was prepared by using the same experimental conditions as those used for the synthesis of (phenol)tricarbonylchromium. Yield: 3.0–4.8 g (51–81%). (2,6-Dimethylphenol)tricarbonylchromium was more air sensitive than the analogous phenol derivative. ^1H NMR (acetone-d_6, 22 °C): δ 2.76 (6 H, s, Me), 5.57 (2 H, d, *m*-Ar, J = 6.3 Hz), 5.17 (1 H, t, *p*-Ar, J = 6.3 Hz). No resonance attributed to dioxane was observed. IR (cm^{-1}, CO region): 1940, 1877.

The same procedure was applied to the preparation of (2,4,6-trimethylphenol)tricarbonylchromium. Yield: 0.5 g (40%). [η-2,4,6-Me$_3$-1-(HO)C_6H_2]Cr(CO)$_3$ is extremely air sensitive. ^1H NMR (acetone-d_6, 22 °C): δ 5.40 (2 H, s, *m*-Ar), 2.02 (6 H, s, *o*-Me), 2.47 (3 H, s, *p*-Me). IR (cm^{-1}, CO region): 1938, 1850.

[Et$_4$N][(η-OC$_6$H$_5$)Cr(CO)$_3$]. In a large Schlenk flask, (phenol)tricarbonylchromium (3.8 g, 16.5 mmol) was slurried with degassed water (200 mL), and an excess of tetraethylammonium hydroxide (11.67 mL, 19.8 mmol) was added via syringe. The yellow solid immediately dissolved, and the solution was stirred for 2 h. The flask was quickly transferred to a rotary evaporator, and the water was removed at 35 °C. The yellow solid residue was dissolved in THF and filtered, and the THF was removed in vacuo. The solid was redissolved in a minimum amount of THF, and the resulting solution was layered with an equal volume of benzene. After waiting for the first few crystals to form at room temperature, the flask was refrigerated at −20 °C, yielding crystals of the product. Yield (crystals): 4.13 g (70%). IR data (cm^{-1}, CO region): 1921, 1823, 1749. ^1H NMR (acetone-d_6, 20 °C) δ 4.52 (1 H, t, *p*-Ar, J = 9.0 Hz), 4.44 (2 H, d, *o*-Ar, J = 6.8 Hz), 5.43 (2 H, t, *m*-Ar, J = 8.0 Hz), 3.50 (3 H, b s, N(CH_2CH$_3$)$_4$), 1.39 (12 H, b s, N(CH$_2$$CH_3$)$_4$. $^{13}C\{^1H\}$ NMR: δ 246 (CO), 164.9 (*i*-Ar), 101.8, 85.5, 17.6 (Ar), 52.9 (N(CH_2CH$_3$)$_4$), 30.3 (N(CH$_2$$CH_3$)$_4$). Anal. Calcd: C, 56.82; H, 7.01; N, 3.90. Found: C, 56.32; H, 7.05; N, 3.92.

[Et$_4$N][(η-2,6-Me$_2$-1-OC$_6$H$_3$)Cr(CO)$_3$]. [Et$_4$N][(η-2,6-Me$_2$-1-OC$_6$H$_3$)Cr(CO)$_3$] was prepared by a procedure analogous to that used for [Et$_4$N][(η-OC$_6$H$_5$)Cr(CO)$_3$]. Yield (crystals): 3.96 g (80%). ^1H NMR (acetone-d_6, 20 °C): δ 1.93 (6 H, s, Me), 5.39 (2 H, d, *m*-Ar, J = 7.9 Hz), 4.47 (1 H, t, *p*-Ar, J = 6.0 Hz), 3.52 (8 H, b s, N(CH_2CH$_3$)$_4$), 1.40 (12 H, b s, N(CH$_2$$CH_3$)$_4$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 20 °C): δ 241 (CO), 163, 131 (*i*-Ar), 102.0, 97.9, (Ar), 52.9 (N(CH_2CH$_3$)$_4$), 7.73 (Ar-Me), 17.9 (N(CH$_2$$CH_3$)$_4$. IR (cm^{-1}, CO region): 1926, 1830, 1808. Anal. Calcd: C, 58.90; H, 7.89; N, 3.62. Found: C, 56.43; H, 7.89; N, 3.47.

[Et$_4$N][(η-2,4,6-Me$_3$-1-OC$_6$H$_2$)Cr(CO)$_3$]. The procedure for preparing (2,4,6-trimethylphenolato)tricarbonylchromium is similar to that used for the synthesis of (phenolato)tricarbonylchromium. The product is extremely air sensitive and is isolated in low yields. ^1H NMR (acetone-d_6, 20 °C): δ 5.36 (2 H, s, *m*-Ar), 2.30 (3 H, b s, *p*-Me), 1.93 (6 H, s, Me), 3.42 (8 H, b s, N(CH_2CH$_3$)$_4$, 1.34 (12 H, b s, N(CH$_2$$CH_3$)$_4$). IR (cm^{-1}, CO region): 1917, 1819, 1803.

[η-(*p*-CH$_3$C$_6$H$_4$SO$_3$)C$_6$H$_5$]Cr(CO)$_3$. In a round-bottom flask, tetraethylammonium (phenolato)tricarbonylchromate (1.9 g, 5.27 mmol) was dissolved in THF (100 mL) and solid *p*-toluenesulfonyl chloride (1.0 g, 5.27 mmol) was slowly added to the solution from an addition tube. After being stirred for 2–3 h, the reaction was filtered and the solvent was removed in vacuo. The yellow residue was dissolved in a minimum of toluene, and an equal volume of hexanes was layered onto the solution. On appearance of the first crystals at room temperature, the flask was refrigerated at −20 °C, yielding crystals of the product. Yield (crystals): 4.05 g (90%). ^1H NMR (acetone-d_6, 23 °C): δ 5.52 (2 H, d, *o*-Ar, J = 6.2 Hz), 5.74 (2 H, t, *m*-Ar, J = 7.5 Hz), 5.34 (1 H, t, *p*-Ar, J = 7.2 Hz), 7.54 and 6.58 (2 H, d, tolyl, J = 4.2 Hz), 2.50 (3 H, s, tolyl-Me). ^{13}C NMR (acetone-d_6, 20 °C): δ 233.0 (CO), 131.6, 130.6, 130.1, 128.4 (tolyl), 128.4, 93.5, 87.0, 69.1 (Ar-Cr(CO)$_3$), 5.0 (Me). IR (cm^{-1}, CO region): 1971, 1883. Anal. Calcd: C, 50.00; H, 3.15. Found: C, 49.70; H, 3.22.

[η^6-2-(Me$_3$Si)-1-(MeC$_6$H$_4$SO$_3$)C$_6$H$_4$]Cr(CO)$_3$. In a Schlenk flask (phenyl tosylate)tricarbonylchromium (0.5 g, 1.30 mmol) was dissolved in THF (17 mL). After the solution was cooled to −78 °C, LDA (0.49 mL, 1.30 mmol) was added via syringe. The color of the solution changed from a dull yellow to light brown. The solution was warmed to −45 °C and the reaction was quenched with Me$_3$SiCl (0.17 mL, 1.30 mmol). The solution was warmed to room temperature and the solvent removed in vacuo. The solid residue was extracted with pentane. The solution was filtered, and the filtrate volume was reduced until the first crystals were observed. Refrigeration at −20 °C yielded crystals of the product. Small quantities (ca 5%) of the title compound were collected. ^1H NMR (acetone-d_6, 20 °C): δ 7.95, 7.60 (2 H, d, tolyl, J = 4.0 Hz), 5.83, 5.54 (1 H, d, Ar, J = 2.6 Hz), 5.21, 5.96 (1 H, t, Ar, J = 5.4 Hz), 2.52 (3 H, s, tolyl), 0.36 (9 H, s, TMS). $^{13}C\{^1H\}$ NMR (acetone-d_6, 23 °C): δ 233.6 (CO), 147.6, 138.7, 133.9, 101.5, 97.1, 94.8, 89.9, 88.3, 84.9 (Ar), 21.6 (Me).

[η-{(*i*-PrO)$_3$Ti}OC$_6$H$_5$]Cr(CO)$_3$. In a Schlenk flask (phenol)tricarbonylchromium (0.5 g, 2.2 mmol) was dissolved in THF, and 1 equiv of tetraisopropoxytitanium was added via syringe. The resulting dark orange solution was evaporated to dryness in vacuo, and the residue was extracted with toluene and filtered. The volume of the solution was drastically reduced to induce the appearance of the first crystals, and the flask was refrigerated at −20 °C. Yields (crystals): 0.63 g (64%). ^1H NMR (benzene-d_6, 20 °C): δ 4.82 (2 H, d, *o*-Ar, J = 3 Hz), 4.72 (2 H, t, *m*-Ar, J = 5.7 Hz), 3.96 (1 H, t, *p*-Ar, J = 5.5 Hz), 4.50 (3 H, sept, OCHMe$_2$, J = 5.9 Hz), 1.20 (18 H, d, OCHMe_2, J = 6.0 Hz). $^{13}C\{^1H\}$ (benzene-d_6, 20 °C): δ 234.7 (Cr(CO)$_3$), 95.4, 92.2, 87.8, 85.0, 84.8, (Ar), 76.9 (OCHMe$_2$) 26.6 (OCHMe_2). IR (cm^{-1}, CO region): 1871, 1959. Mass spectrum: m/e 454 (M$^+$), 370 (M$^+$ − 3CO), 318 (M$^+$ − Cr(CO)$_3$), 225 (M$^+$ − Ti(O-*i*-Pr)$_3$). Anal. Calcd: C, 47.58; H, 5.77. Found: C, 47.05; H, 6.01.

[η-2,6-Me$_2$-1-{(*i*-PrO)$_3$TiO}C$_6$H$_3$]Cr(CO)$_3$. The same general procedure used for the synthesis of [η-{(*i*-PrO)$_3$TiO}C$_6$H$_5$]Cr(CO)$_3$ was used for preparation of the 2,6-dimethyl isomer, substituting (2,6-dimethylphenol)tricarbonylchromium for (phenol)tricarbonylchromium. Yield (crystals): 0.64 g (63.7%). ^1H NMR (benzene, 20 °C); δ 2.11 (6 H, s, CH$_3$), 4.62 (2 H, d, *m*-Ar, J = 6.3 Hz), 4.31, (1 H, t, *p*-Ar, J = 6.3 Hz), 4.52 (3 H, sept, OCH(Me)$_2$, J = 6 Hz), 1.20 (18 H, d, OCH(Me)$_2$, J = 6 Hz). ^{13}C NMR (benzene-d_6, 20 °C, partial): δ 94.13, 87.95 (Ar), 26.34, (OCHMe$_2$), 16.75 (OCHMe_2). IR (cm^{-1}, CO region): 1950, 1865.

---

[7] (a) Chandra, G.; Lappert, M. F. *J. Chem. Soc. A* **1968**, 1940. (b) Fischer, E. O.; Ofele, K.; Essler, H.; Frohlich, W.; Mortensen, P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763.

Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$. In a Schlenk flask Cp$_2$Zr(NMe$_2$)$_2$ (1.0 g, 3.2 mmol) was dissolved in THF (12 mL), and [η-(HO)C$_6$H$_5$]Cr(CO)$_3$ (1.5 g, 6.4 mmol) was added slowly from an addition tube. The reaction was stirred for 2 h and the solvent removed in vacuo. The product was extracted with a minimum volume of toluene, the volume of solvent was drastically reduced, and the product was crystallized at −20 °C. Yield (crystals): 0.88 g (60%). ^{1}H NMR (acetone-d_6, 20 °C): δ 4.50 (2 H, d, *o*-Ar, J = 3.2 Hz), 4.89 (2 H, *t*, *m*-Ar, J = 6.7 Hz), 4.07 (1 H, t, *p*-Ar, J = 6.3 Hz), 5.88 (5 H, s, Cp). ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C): δ 234.9 (Cr(CO)$_3$), 136.2 (Cp), 114.3, 96.2, 84.0, 83.1 (Ar). IR (cm^{-1}, CO region): 1857, 1948. Mass spectrum: m/e 594 (M$^+$ − 3CO), 542 (M$^+$ − Cr(CO)$_3$). Anal. Calcd: C, 49.48; H, 2.97. Found: C, 49.43; H, 2.96.

Crystallographic Study. A suitably sized crystal of Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$ was mounted in a glass capillary under a stream of dry nitrogen gas. The ends of the capillary were sealed with wax, and the capillary was mounted at ambient temperature. Cell constants were determined by using 15 reflections widely scattered throughout reciprocal space. Preliminary data indicated an orthorhombic cell with systematic absences, 0*kl* for $k + 1 = 2n + 1$ and *hk*0 for $h = 2n + 1$, identifying the space group as either *Pnma* or *Pn*2$_1$*a*. The centrosymmetric space group *Pnma* was selected by inspection of the Patterson map, and this assignment was confirmed by the structure refinement. Data were collected through two octants of space (to $2\theta = 100°$) on a Syntex P2$_1$ diffractometer using a θ–2θ scan procedure. Two reflections were monitored every 100 measurements for intensity changes, and a correction for a 5% reduction in intensity was applied. A semiempirical ψ-scan technique was used to correct for absorption (correction factor 0.955–1.045). Reflections with $F_o^2 < 0.20(F_o^2)$ were reset to $F_o^2 = 0.20(F_o^2)$. The $\sigma(F_o^2)$ and $\sigma(F_0)$ values were defined as $\sigma(F_o^2) = [\sigma^2\text{count} + (0.02F_o^2)^2]^{1/2}$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. R(int) for merging the two octants of collected data was 0.089. A total of 1403 independent F_o data were used for the structure determination and refinement, and the structure was solved by the heavy-atom method. Anomalous dispersion corrections were used for the Zr and Cr atoms. All hydrogen atoms were located in a difference electron density map and were introduced into the refinement with isotropic thermal paramters. The $\sum w(|F_o| - |F_c|)^2$ was minimized, for $w = 1/\sigma(F_o)^2$. All non-hydrogen atoms were subjected to an anisotropic refinement. The refinement was converged to $R = 0.078$, $R_w = 0.089$, and $S = 1.151$. The largest peak found in the final difference Fourier map was near the Zr atom (+0.81 e/Å^3). Atomic scattering factors were taken from ref 27. All calculations were performed on a VAX/8650 computer at the University of Kansas using programs of the KUDNA system (Takusagawa, 1984). A summary of the experimental details is collected Table I.

Results and Discussion

Preparation and Structure of (η-Aryloxide)Cr(CO)$_3$ Complexes. The [(η-aryloxide)Cr(CO)$_3$]$^-$ complexes can be prepared through the reaction of parent (η-phenol)Cr(CO)$_3$ complexes with various bases (RLi, NaOH, R$_4$NOH) in both aqueous and nonaqueous media (eq 1).

$$[\eta\text{-(HO)C}_6\text{H}_5]\text{Cr(CO)}_3 + \text{MB} \xrightarrow{\text{solvent, 20 °C}} \text{M}[(\eta\text{-OC}_6\text{H}_5)\text{Cr(CO)}_3] + \text{HB} \quad (1)$$

$$\text{MB} = \text{RLi, solvent} = \text{Et}_2\text{O; MB} = \text{NaOH, [Et}_4\text{N]OH, solvent} = \text{H}_2\text{O}$$

The aryloxide anions are conveniently prepared as the crystalline Et$_4$N$^+$ salts by reaction of the parent phenol derivative with aqueous [Et$_4$N]OH, dissolving the resulting crude product in THF and inducing crystallization through addition of a nonpolar cosolvent. The resulting phenoxide and 2,6-dimethylphenoxide molecules are yellow crystalline materials that are extremely soluble in water, THF, and acetone. Both of these molecules are reasonably air sensitive, decomposing to green residues after several hours in solution. The corresponding 2,4,6-trimethylphenoxide salt was never fully characterized. Although its precursor mesitol complex reacted with degassed aqueous [Et$_4$N]OH, the resulting yellow solutions rapidly deposited copious quantities of intractable green solid, which was assumed to be a byproduct of the oxidation of the chromium center.

Table I. Summary of Crystal Data for Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$

empirical formula	ZrCr$_2$C$_{28}$H$_{20}$O$_8$
color of cryst	yellow-brown
cryst dimensions, mm	0.07 × 0.05 × 0.03
space group	*Pnma*
cell dimens (25 °C)	
a, Å	15.023 (3)
b, Å	21.864 (5)
c, Å	8.073 (2)
Z, molecules/cell	4
V, Å^3	2652 (1)
d(calcd), g/cm^3	1.702
X-ray radiatn	Cu Kα (λ = 1.5418 Å)
MW	679.67
linear abs coeff, cm^{-1}	108.0
av ω scan width, deg	0.3
scan speed, deg/min	1.0–20.0
scan width, deg + dispersn	1.2 below Kα and 1.2 above Kα
bkgd range	$^1/_6$ of scan at edges
aperture size, mm	0.5
2θ range, deg	4–100
total no. of reflctns collected	2472
no. of unique intensities	1403
$R(F)$	0.078
$R_w(F)$	0.089
goodness of fit for last cycle	1.151
Δ/σ for last cycle	0.11

The ^{1}H and ^{13}C NMR spectra of the [(η-phenoxide)Cr(CO)$_3$]$^-$ moiety are consistent with the adoption of an η^6-arene bonding mode by the arene ligand, as opposed to the alternate possible η^5-cyclohexadienone structure. Chemical shifts for ortho hydrogens in η^6-structures typically fall between δ 4.5 and δ 5.5 in acetone-d_6, while "ortho" hydrogens in the η^5-structure typically fall between δ 3.0 and δ 2.0.[8,9] The ortho hydrogens of the [(η-phenoxide)Cr(CO)$_3$]$^-$ fall at δ 4.54, near the high end of the range for the η^6-complexes. This observation is reinforced by the IR spectrum of the compound, which displays the expected CO stretching bands of virtual A and E symmetry at ν (cm^{-1}) = 1923 and 1799 (1828), respectively. The CO stretching bands of bonafide cyclohexadienide complexes, in which a formal 1− charge resides on the Cr(CO)$_3$ fragment, typically contain one mode near 1710 cm^{-1}, far below the normal range for neutral Cr(CO)$_3$ fragments. The adoption of an η^6-structure by the π-aryloxide chromium complexes (**3**) superficially appears to run counter to structural features generally observed for both chromium arene complexes and other π-metallocene complexes.[10,11] Neutral π-metallocene half-sandwich molecules with potential terminal oxo-anion substituents prefer to adopt the alternate keto structure (**4** and **5**).[10,11] In addition, all of the fully characterized π-arene chromium complexes that bear a formal negative charge at a benzylic carbon center adopt the η^5-pentadienide olefin structure.[10] Contrary to this trend, the [(η-{(CO)$_n$M}C$_6$H$_5$)Cr(CO)$_3$]$^-$ (M = Cr, W, n = 5; M = Fe, n = 4) complexes, in which the formal negative charge is borne by the M(CO)$_n$ fragment α to the

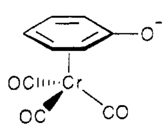
---

(8) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

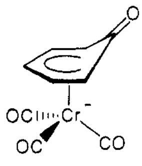
(9) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifugi, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 5535.

(10) Reike, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699.

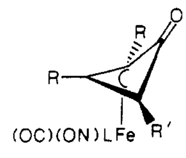
(11) (a) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1754. (b) Hughes, R. P.; Klaui, W.; Reisch, J. W.; Muller, A. *Ibid.* **1985**, *4*, 1761. (c) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Ibid.* **1984**, *3*, 1761.



3



4



5

arene ligand, adopts the same η^6-structure found for the phenoxide complex.[12] The observed structures of the $[(\eta^6\text{-}OC_6H_5)Cr(CO)_3]^-$ and $[(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]^-$ molecules demonstrate the limited capacity of the $Cr(CO)_3$ unit to delocalize negative charge α to the arene, particularly when the α-substituent is a highly electronegative atom or a π-acceptor-substituted transition-metal center. We can speculate that were the $Cr(CO)_3$ fragment replaced by a stronger electron acceptor fragment, such as $Mn(CO)_3^+$,[13] the phenoxide structure might convert to the η^5-cyclohexadienone form.

Reactivity of the π-Aryloxide Metal Anions. The chromium aryloxide anions react readily with p-toluenesulfonyl chloride to form (η-phenyl tosylate)$Cr(CO)_3$ complexes in ether solvents (eq 2). While the η-phenyl tosylate

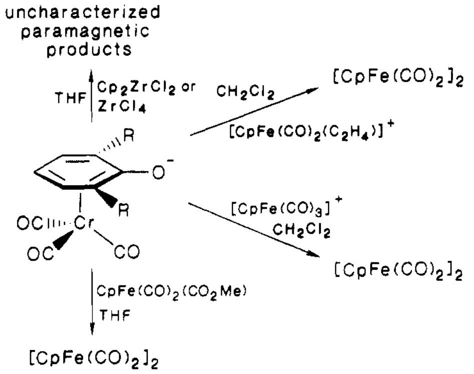
$$[\eta\text{-}(OC_6H_5)Cr(CO)_3]^- + p\text{-}MeC_6H_4SO_2Cl \rightarrow [\eta\text{-}(p\text{-}MeC_6H_4SO_2)OC_6H_5]Cr(CO)_3 + Cl^- \quad (2)$$

derivative can be isolated in modest yield as a yellow thermally stable molecule, the (η-2,6-dimethylphenyl tosylate)$Cr(CO)_3$ derivative decomposes rapidly at ambient temperature both in solution and in the solid state and can therefore only be identified spectroscopically. The more common route to π-arene chromium complexes would proceed through a direct reaction between the parent arene derivative (in this case phenyl tosylate or 2,6-dimethylphenyl tosylate) and $Cr(CO)_6$ in refluxing ether solvent.[14] These direct reactions resulted in the complete consumption of the chromium hexacarbonyl and phenyl tosylate reagents, but failed to produce an isolable η^6-arene adduct. This may be caused by the reduction of the sulfonate group by the Cr(0) center, in a manner analogous to the reduction of nitro aromatics to diazoarenes by $Cr(CO)_6$.[15] Reactions between $[\eta\text{-}(HO)C_6H_5]Cr(CO)_3$ and p-$MeC_6H_4SO_2Cl$ in the presence of pyridine also failed to produce the anticipated tosylate chromium complex, resulting instead in the formation of $Cr(CO)_3(py)_3$.

The product (phenyl tosylate)tricarbonylchromium complex is characterized by a shift of the CO stretching bands of the $Cr(CO)_3$ unit to 1971 and 1883 cm^{-1}, higher than the corresponding bonds in (phenol)tricarbonylchromium at 1928 and 1841 cm^{-1}. This trend agrees with the poorer π-donor ability of the tosyl group as compared with the OH group. Taken together with the CO stretching frequencies of the $[(\eta\text{-}OC_6H_5)Cr(CO)_3]^-$ substituent, the three compounds conform to the expected trend for π-donor ability: $O^- \gg OH > OTs$. It is also noteworthy that changing to weaker π-donor groups exhibits the greatest effect on the chemical shift of the o-arene hydrogen atoms, shifting them from δ 4.59 in the η-phenoxide complex to δ 5.52 in the η-phenyl tosylate complex.

The $[(\eta\text{-}OC_6H_5)Cr(CO)_3]^-$ complex also reacts readily with trifluoroacetic anhydride in ether and acetone to form a yellow $[\eta\text{-}(CF_3CO)OC_6H_5]Cr(CO)_3$ complex which is stable below 0 °C in solution. Because the complex rapidly decomposes, changing to a lime green color and eventually depositing green solid from solution, the progress of this reaction was followed exclusively by ^1H and ^{13}C NMR spectroscopy.[16]

Scheme I



Although reactions between π-aryloxide chromium complexes and highly activated organic electrophiles proceeded readily, reactions with bulkier, less potent electrophiles were disfavored. For example, $[(\eta\text{-}OC_6H_5)Cr(CO)_3]^-$ failed to react with $(\eta\text{-}ClC_6H_5)Cr(CO)_3$ over several days of refluxing in THF to produce the phenyl ether complex $[(\eta\text{-}C_6H_5)Cr(CO)_3]_2O$.

The metal aryloxide anions also fail to react in the anticipated manner with a variety of metal halides and transition metal electrophiles (Scheme I). Reactions between Cp_2ZrCl_2 or $ZrCl_4$ and either the η^6-phenoxide or η^6-2,6-dimethylphenoxide derivatives resulted in the disruption of the arene phenolate complex, together with the complete consumption of the metal halide material. The aryloxide complexes also react with both $[CpFe(CO)_3][BF_4]$ and $CpFe(CO)_2(CO_2Et)$ to produce $[CpFe(CO)_2]_2$ as the only characterizable organometallic product. The propensity of $[CpFe(CO)_3]^+$ to react via electron-transfer pathways,[17] taken together with the broad ^1H NMR resonances observed in the of product mixtures from reactions of both the iron and zirconium electrophiles, indicates that the $[(\eta\text{-aryloxide})Cr(CO)_3]^-$ chromium complexes may be consumed in electron-transfer reactions with the metal electrophiles.

Reactions of $[\eta^6\text{-}(p\text{-}MeC_6H_4SO_2)OC_6H_5]Cr(CO)_3$ with Nucleophiles and Bases. Potent metal carbonyl nucleophiles such as $[CpFe(CO)_2]^-$ show no evidence of reaction with phenyl tosylate or phenyl trifluoroacetate chromium complexes in THF at ambient temperature. Likewise, carbon based nucleophiles such as Na[diethyl malonate] and Li[butyrylnitrile], which are known to effect the nucleophilic displacement of halide anions, produce no detectable change in THF solutions of the chromium substrates over several days at ambient temperature. These results appear to indicate that although the p-$MeC_6H_4SO_3$ and CF_3CO_2 groups are poorer π-donors than groups such as the methoxide unit, the accompanying reduction in bond strength is clearly insufficient to allow the desired nucleophilic displacement of the oxo leaving group. The steric hindrance engendered by the ap-

---

(12) Thomas-Miller, M. E.; Heppert, J. A.; Scherubel, D. M., submitted for publication.

(13) Knipe, A. C.; McGuinness, S. J.; Watts, W. E. *J. Organomet. Chem.* **1979**, *172*, 463.

(14) Kirtley, S. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 3, p 975.

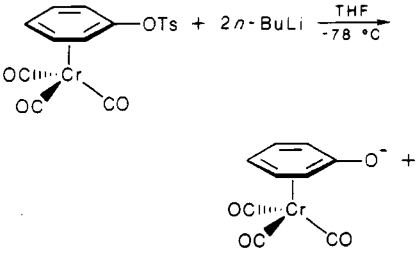
(15) Knipe, A. C.; McGuinness, S. J.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1981**, 193.

(16) The reaction was performed by placing a weighed quantity of $[Et_4N][(\eta\text{-}OC_6H_5)Cr(CO)_3]$ into an NMR tube, adding acetone-d_6 (approximately 0.6 mL), and sealing the tube with a cerum cap. After the tube was cooled to -40 °C, a stoichiometric quantity of $(CF_3CO)_2O$ was added to the tube through the cerum cap via syringe. Changes on the ^1H and ^{13}C NMR spectra of the sample at -40 °C were consistent with the formation of $[\eta\text{-}(CF_3CO)OC_6H_5]Cr(CO)_3$.

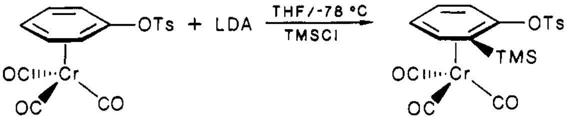
(17) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.

proaching nucleophile and the tosyl or trifluoroacetate substituent will probably be greater than that encountered by the same nucleophile attacking a carbon–halogen bond, and this may also retard the rate of nucleophilic substitution. The aromatic carbon centers are, as expected, still susceptible to nucleophilic attack because Li[dithiane] readily adds to the (η-phenyl tosylate)Cr(CO)$_3$ complex to produce a complex mixture of compounds. The identities of these products are currently under investigation.

Scheme II

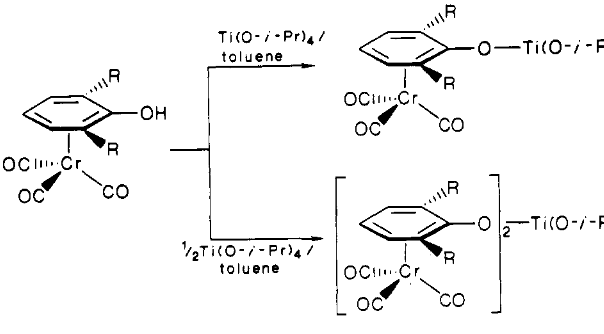


The [η-(p-MeC$_6$H$_4$SO$_2$)OC$_6$H$_5$]Cr(CO)$_3$ molecule reacts with lithium alkyl bases, forming products whose identities depends on the base used. The (η-phenyl tosylate)Cr(CO)$_3$ complex reacts with 2 equiv of n-BuLi in ether at −40 °C to produce Li[(η-OC$_6$H$_5$)Cr(CO)$_3$] as the only isolable organometallic product. We hypothesize that, in accordance with the high relative nucleophilicity and potential reducing power of n-BuLi, that the tosylate derivative is cleaved into (η-phenoxide)Cr(CO)$_3$ and sulfenium anions (Scheme II). A less highly nucleophilic base, LDA (lithium diisopropyl amide), reacts with the phenyl tosylate complex to produce an (η-o-Li{O–tosylate}C$_6$H$_4$)Cr(CO)$_3$ which was readily converted to the o-Me$_3$Si derivative on addition of Me$_3$SiCl (eq 3). This result was anticipated based on the ability of other heteroatom substituents (including OMe, Cl, and F) to act as ortho directing groups for lithiation.[18,19] The product decomposed rapidly on exposure to air or on standing for several hours in solution at ambient temperature.



(3)

Alcoholysis Reactions of (η-Phenol)Cr(CO)$_3$ Derivatives. The (η-phenol)Cr(CO)$_3$ complexes are readily substituted onto early-transiton-metal centers through alcoholysis reactions. For example, the phenol and 2,6-dimethylphenol complexes react stoichiometrically to replace either one or two of the isopropoxide ligands of Ti(O-i-Pr)$_4$ (eq 4 and 5). The products are isolated as air- and moisture-sensitive yellow-orange crystals and are soluble in alkane, ether, and aromatic solvents. The [(η-aryloxide)Cr(CO)$_3$]Ti(O-i-Pr)$_3$ complexes are apparently more stable in solution, as evidenced by the slow decomposition of the [η-(OAr)Cr(CO)$_3$]$_2$Ti(O-i-Pr)$_2$ (Ar = C$_6$H$_5$ or 2,6-Me$_2$C$_6$H$_3$) complexes in solution over several hours. The identity of the decomposition products has not yet been determined.



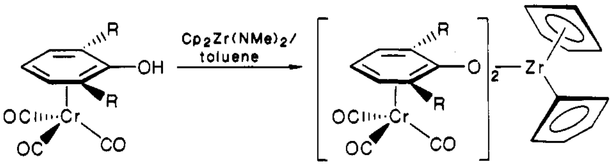
(4)

(5)

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$

atom	x	y	z	B, Å^2
Zr(1)	0.46211 (6)	0.75	0.6691 (1)	2.53
Cr(1)	0.62344 (9)	0.56976 (6)	0.3461 (2)	2.84
O(B)	0.5284 (4)	0.6823 (3)	0.5588 (8)	5.36
C(1)	0.5998 (6)	0.6484 (4)	0.532 (1)	3.71
C(2)	0.6105 (6)	0.5920 (4)	0.615 (1)	3.52
C(3)	0.6874 (5)	0.5575 (5)	0.590 (1)	3.91
C(4)	0.7527 (6)	0.5761 (4)	0.479 (1)	4.09
C(5)	0.7381 (7)	0.6287 (4)	0.387 (1)	4.53
C(6)	0.6620 (6)	0.6650 (4)	0.415 (1)	4.38
C(7)	0.6167 (6)	0.4870 (4)	0.324 (1)	3.96
C(8)	0.6504 (7)	0.5733 (4)	0.126 (1)	4.57
C(9)	0.5057 (6)	0.5745 (4)	0.296 (1)	4.03
O(7)	0.6113 (5)	0.4350 (5)	0.301 (1)	6.47
O(8)	0.6655 (7)	0.5746 (3)	−0.0152 (9)	7.19
O(9)	0.4304 (5)	0.5776 (4)	0.266 (1)	6.76
C(10)	0.3020 (7)	0.7840 (5)	0.658 (1)	5.29
C(11)	0.3358 (6)	0.8020 (5)	0.516 (1)	4.81
C(12)	0.360 (1)	0.75	0.425 (3)	5.96
C(13)	0.5598 (7)	0.7806 (5)	0.910 (1)	5.10
C(14)	0.4746 (8)	0.6994 (6)	0.945 (1)	5.64
C(15)	0.422 (1)	0.75	0.965 (2)	5.34
H(5)	0.580 (8)	0.588 (5)	0.68 (1)	5.71
H(6)	0.695 (7)	0.519 (5)	0.66 (1)	5.79
H(7)	0.797 (6)	0.548 (4)	0.468 (9)	4.01
H(8)	0.772 (5)	0.632 (3)	0.313 (8)	1.52
H(9)	0.640 (6)	0.691 (4)	0.34 (1)	4.28
H(10)	0.279 (5)	0.797 (3)	0.744 (9)	2.76
H(11)	0.348 (7)	0.839 (5)	0.45 (1)	6.16
H(12)	0.376 (8)	0.75	0.36 (1)	1.57
H(13)	0.623 (9)	0.816 (6)	0.88 (2)	11.97
H(14)	0.456 (5)	0.671 (3)	0.953 (9)	1.64
H(15)	0.382 (8)	0.75	1.00 (1)	2.42

Cp$_2$Zr(NMe$_2$)$_2$[7a] also reacts with 2 equiv of [η-(HO)C$_6$H$_5$]Cr(CO)$_3$ to produce high yields of a yellow crystalline Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$ (eq 6). Stoichiometric reactions between Cp$_2$Zr(NMe$_2$)$_2$ and [η-(HO)C$_6$H$_5$]Cr(CO)$_3$ resulted exclusively in the isolation of the disubstituted product. This behavior is observed in the alcoholysis behavior of other Cp$_2$ZrX$_2$ derivatives.[20] Reaction between Cp$_2$Zr(NMe$_2$)$_2$ and [η-(HO)-2,6-Me$_2$C$_6$H$_3$]Cr(CO)$_3$ failed to produce a pure mono- or bis-substituted zirconium product, and we speculate that the Zr center activates the benzylic hydrogens of the arene methyl groups, circumventing formation of the bis(chromium aryloxide) product.



(6)

X-ray Crystal Structure of Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$. An ORTEP representation showing an oblique view of Cp$_2$Zr[(η-OC$_6$H$_5$)Cr(CO)$_3$]$_2$ and the atom numbering scheme is shown in Figure 1, while the fractional coordinates and isotropic thermal parameters for this molecule in addition to selected bond distances and angles are collected in Tables II and III, respectively. The structure

---

(18) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(19) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768.

(20) Weber, L.; Meine, G.; Boese, R.; Augart, H. *Organometallics* **1987**, *6*, 2484.

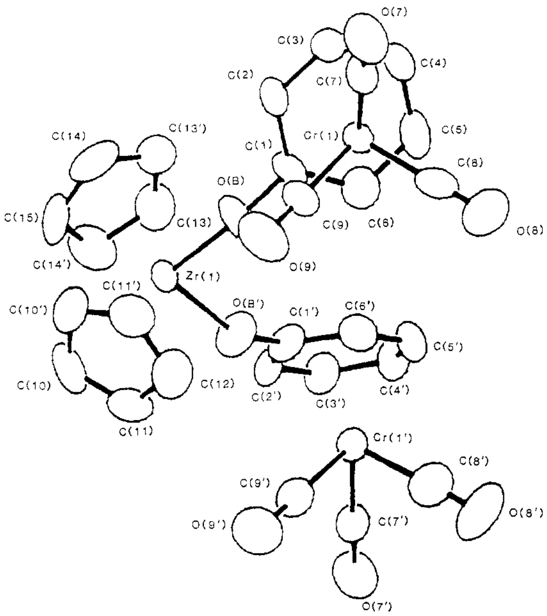


Figure 1. ORTEP representation of the X-ray crystal structure of $Cp_2Zr[(\eta^6\text{-}OC_6H_5)Cr(CO)_3]_2$ showing an oblique view of the molecule with the atom-numbering scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Zr[(\eta\text{-}OC_6H_5)Cr(CO)_3]_2$[a]

Zr(1)–O(B)	1.992 (6)	Cr(1)–C(4)	2.223 (9)
Zr(1)–C_{Cp}	2.50 (av)	Cr(1)–C(5)	2.176 (10)
Zr(1)–CP(1)	2.230 (1)	Cr(1)–C(6)	2.232 (10)
Zr(1)–CP(2)	2.215 (1)	Cr(1)–$C_{carbonyl}$	1.82 (av)
Cr(1)–C(1)	2.310 (8)	Cr(1)–PH(1)	1.739 (1)
Cr(1)–C(2)	2.233 (10)	O(B)–C(1)	1.323 (10)
Cr(1)–C(3)	2.207 (8)		
O(B)–Zr(1)–O(B′)	95.82 (26)	C(1)–Cr(1)–C(8)	129.46 (33)
O(B)–Zr(1)–CP(1)	105.61 (17)	C(1)–Cr(1)–C(9)	87.28 (35)
O(B)–Zr(1)–CP(2)	108.11 (18)	Zr(1)–O(B)–C(1)	153.55 (56)
CP(1)–Zr(1)–CP(2)	128.72 (4)	Cr(1)–C(1)–O(B)	130.49 (59)
C(1)–Cr(1)–C(7)	142.64 (33)	Cr(1)–C–$O_{carbonyl}$	177.8 (av)

[a] CP and PH represent the calculated centroids for the cyclopentadienide and phenyl rings, respectively.

of the bis(η-phenoxide) derivative was simplified by the presence of a crystallographic mirror plane that bisects the O(B)–Zr(1)–O(B′) angle and contains the C(10) and C(13) atoms of the two cyclopentadienide ligands. The presence of this mirror plane is more readily seen by the view of the molecule down the vector connecting the centroids of the two staggered cyclopentadienide ligands, shown in Figure 2.

The Cp_2Zr fragment adopts a staggered bent metallocene structure in which both of the Cp rings are bisected by a crystallographic mirror plane. The Cp(cent)–Zr(1)–Cp(cent) angle of 128.72 (4)° falls in the range between 128.5° and 129.5° that is typical of other Cp_2ZrXY complexes, when X and Y are carbon, chlorine, or oxygen substituents.[21] It is interesting to note that the molecule exhibits a rarely observed difference in the two Zr–Cp(cent) bond distances, Zr(1)–CP(1) = 2.230 (1) Å and Zr(1)–CP(2) = 2.215 (1) Å. The longer Zr(1)–CP(1) distance represents the cyclopentadienide ring distal to the $Cr(CO)_3$ units and probably reflects an effort to avoid steric contact between the Cp and $Cr(CO)_3$ groups. The O(B)–Zr(1)–O(B′) angle of 95.8(3)° again falls within the normal range from 95.8° to 97.1° for zirconium bent-sandwich molecules.[21] This value belies the suggestion that the (η-OC_6H_5)$Cr(CO)_3$ units engender significant mutual steric repulsion because complexes that exhibit such steric interactions typically show an expanded X–Zr–Y angle of between 101° and 105°.[22]

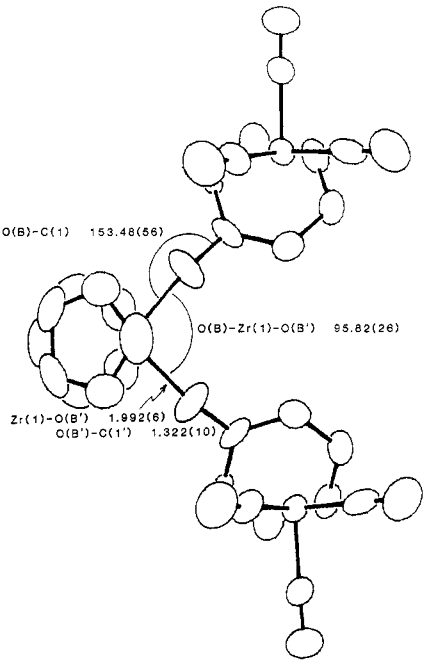


Figure 2. A view of $Cp_2Zr[(\eta\text{-}OC_6H_5)Cr(CO)_3]_2$ down the vector between the centroids of the staggered rings, showing the relative position of the (η-OC_6H_5)$Cr(CO)_3$ units and bond distances and angles within the O–Zr–O core.

The (η-OC_6H_5)$Cr(CO)_3$ subunit also exhibits many features common to (η-arene)$Cr(CO)_3$ derivatives in which the arene bears strong π-donor substituents.[1e,23] The $Cr(CO)_3$ fragment occupies a virtual syn-eclipsed conformation (6), being skewed by 9.4° away from the Cp_2Zr core to allow the carbonyl eclipsing the C(1)–O(B) bond to avoid steric contact with the Zr center. The syn-eclipsed conformation is favored for molecules bearing π-donor ligands because it allows the carbonyl ligands trans to the ortho carbon centers to derive the maximum π-back-donation from dπ orbitals that overlap with the more negatively charged ortho carbons.[24] All of the C_{arene}–Cr(1) distances are identical within statistical error, except the distance to the carbon center bearing the oxygen substituent. The slight increase in this distance (0.09 Å) over the other C_{arene}–Cr distances, together with the slightly shortened C(1)–O(B) bond length of 1.323 (10) Å, suggests that the arene unit has developed some C–O multiple-bond character, consistent with the ability of the $Cr(CO)_3$ fragment to stabilize such interactions. The lengthening of the Cr(1)–C(1) distance does not, in fact, stem from a concomitant lengthening of the arene C(1)–C(2) and C(1)–C(6) bonds but originates in the elevation of the C(1)–O(B) vector by 3.7° above the least-squares plane of the arene. These structural features suggest that a small amount of the Meisenheimer-like resonance form 7 is mixing with the anticipated structure 8 to produce the ground-state

---

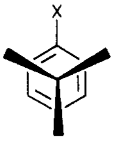
(21) (a) Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79. (b) Prout, K.; Cameron, S. T.; Border, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect B.* **1974**, *30*, 2290. (c) Barger, P. T.; Sanatarsilro, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178 and references therein.

(22) (a) Jinbi, D.; Meizhen, L.; Jiping, Z.; Shoushau, C. *J. Struct. Chem.* **1982**, *1*, 63. (b) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654.

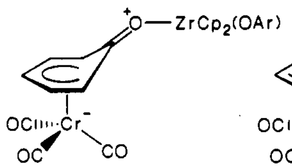
(23) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(24) Semmelhack, M. F.; Garcia, J. L.; Cordes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467.

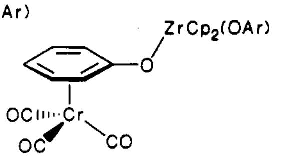
structure of the molecule, although it should be noted that the overall contribution of **7** is very small.



6



7



8

As we might have inferred from the discussion above, extremely little character from a Zr(1)–O(B) multiply bonded valence structure (**4**) contributes to bonding in the $Cp_2Zr(OAr)_2$ core. The O(B′)–Zr(1)–O(B)–C(1) dihedral angle of 155.3° is far from the optimal 90° angles required for π-bonding to the **2a**, LUMO of the Cp_2Zr fragment.[25] In addition, the observed Zr(1)–O(B)–C(1) angle of 153.6° is close to the values of Zr–O–C angles found in $Cp_2Zr(OR)_2$ complexes that display some steric repulsion between the alkoxide ligands but have little or no Zr–O π-bonding.[21,22] For example, this value does not approach the Zr–O–Zr and Zr–O–R angles of 161.1° and 177.3° observed in instances of strong π-bonding in the O–Zr–O core.[25]

Conclusion. The (η-aryloxide)Cr(CO)$_3$ complexes formed from the reaction of the corresponding [η-(HO)-Ar]Cr(CO)$_3$ derivatives with base react with potent organic electrophiles to form new carboxylate- and sulfonate-substituted π-arene complexes. These products are not subject to nucleophilic displacement of the oxo moiety, although they do react with lithium alkyl bases to form products of reduction or deprotonation. While sulfonate and (trifluoromethyl)carbonylate derivatives of the phenoxide anions show no propensity for displacement of the oxo leaving group by metal nucleophiles, a variety of early transition metal substituted phenoxide chromium complexes are accessible through alcoholysis reactions. The η-phenoxide chromium ligands appear to enforce some unique structural features in the new complexes, and our efforts to define the scope of these new influences are the subject of further studies.

Acknowledgment. We thank the University of Kansas General Research Fund and The Research Corp. for a Cottrell Research Grant in support of this Project.

Registry No. [η-(HO)C_6H_5]Cr(CO)$_3$, 32802-03-2; [η-2,6-Me_2-1-(HO)C_6H_3]Cr(CO)$_3$, 117688-93-4; [η-2,4,6-Me_3-1-(HO)C_6H_2]Cr(CO)$_3$, 117688-94-5; [Et_4N][(η-OC_6H_5)Cr(CO)$_3$], 117688-95-6; [Et_4N][η-2,6-Me_2-1-OC_6H_3)Cr(CO)$_3$], 117688-97-8; [Et_4N][η-2,4,6-Me_3-1-OC_6H_2)Cr(CO)$_3$], 117688-99-0; [η-(*p*-$CH_3C_6H_4SO_3$)C_6H_5]Cr(CO)$_3$, 117689-00-6; [η-2-(Me_3Si)-1-($MeC_6H_4SO_3$)C_6H_4]Cr(CO)$_3$, 117689-01-7; [η-(i-PrO)$_3TiOC_6H_5$]-Cr(CO)$_3$, 117689-02-8; [η-2,6-Me_2-1{(*i*-Pr-O)$_3$TiO}C_6H_3]Cr(CO)$_3$, 117689-03-9; $Cp_2Zr(NMe_2)_2$, 11108-30-8; Cp_2Zr[(η-OC_6H_5)Cr-(CO)$_3$]$_2$, 117689-04-0; phenol, 108-95-2; 2,6-dimethylphenol, 576-26-1; 2,4,6-trimethylphenol, 527-60-6; chromium hexacarbonyl, 13007-92-6; tetraethylammonium hydroxide, 77-98-5; tetraisopropoxytitanium, 546-68-9.

Supplementary Material Available: Complete tables of X-ray crystallographic data, including fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (27 pages); a $F_o - F_c$ list (9 pages). Ordering information is given on any current masthead page.

---

(25) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(26) (a) Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1983**, *23*, 243. (b) Strezowski, J. J.; Eick, H. A. *J. Am. Chem. Soc.* **1969**, *91*, 2890. (c) Von Dreele, R. B.; Strezowski, J. J.; Fay, R. C. *Ibid.* **1971**, *93*, 2887. (d) Quingdivan, Y.; Xianglin, J.; Xiaojie, X.; Genzei, L.; Yougi, T.; Shoushan, C. *Sci. Sin., Ser. B* **1982**, *25*, 356. (e) Chun, H. K.; Steffan, W. L.; Fay, R. C. *J. Am. Chem. Soc.* **1979**, *18*, 2458.

(27) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.