

Synthesis and Structure–Property Relationships in $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ Chemistry

From Guided Experiments to Discovery Research

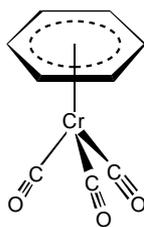
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Background and Rationale

An emerging trend in the design of new laboratory experiments is to choose ones that provide a student experience that as closely as possible duplicates the research experience. One approach to making this experience more authentic is to ensure that no two students in a class and, ideally, no two classes over a student generation (i.e., several years) prepare the same product. A series of target molecules having the same basic structure but different substituents is ideal for these purposes. Unfortunately, each additional reagent purchased to give the students variety also rapidly increases total lab costs. Thus, as many of the reagents as possible for any new discovery research project should already be available in the departmental chemical inventory. Since any instructor's time to validate new experimental procedures is limited, the series of target syntheses should have closely related reaction conditions and the factors that affect reaction conditions, yield, and product purification and identification should be well understood. Experience has also shown that students tend to have more confidence and learn more from each other if teams of students or the whole class work on related reactions at the same time. Unfortunately, this is difficult if expensive specialized glassware and equipment are required. An additional benefit of having each student prepare a different but related derivative is that students can be asked to compare their results and develop structure–property correlations.

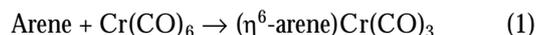
$(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ complexes (see inset) have been extensively described in the literature (1, 2) and are discussed in most courses dealing with transition-metal organometallic chemistry. This interest arises both from both the fascinating theoretical, spectroscopic, structural, and reactivity properties of these molecules and their application to applied areas as varied as transition metals in organic synthesis and organometallic polymer chemistry (1, 2). They would seem to be ideal candidates for the inorganic or organic synthesis lab, since they are relatively simple and inexpensive to prepare; they are only moderately air sensitive; and they can be prepared for a wide range of arenes (1). Indeed, a congeneric complex, $(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)\text{Mo}(\text{CO})_3$, has been a standard in the inorganic lab for several decades (3, 4). Nevertheless, the chromium complexes have not been as widely utilized in teaching labs as they could be. In this paper, we suggest the use of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$



complexes in the inorganic laboratory for guided experiments, discovery research/cooperative learning labs (5), and special projects.

Syntheses of the $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ Complexes

$(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ complexes have been prepared by a wide variety of methods. In our hands, the simplest and most general is the thermal reaction of $\text{Cr}(\text{CO})_6$ and the arene of choice in an ether solvent:



For arenes that are relatively electron rich and have a predominance of R, OR, and NR_2 (where R = H, alkyl, or aryl) substituents but no more than one electron-withdrawing halogen, CO_2R , or CF_3 substituent, these reactions are generally very clean and proceed to completion in from about three hours to about three days. Overnight reaction times are almost always sufficient for the aniline derivatives, especially when a 2- to 4-fold excess of $\text{Cr}(\text{CO})_6$ is employed.¹ For most arenes, such syntheses are best carried out in a 9:1 mixture of di-*n*-butyl ether and tetrahydrofuran (1a, 6). For electron-poor arenes, the reaction times are longer (typically several days to a week) and ideal reaction conditions are more varied. However, dioxane generally appears to be the best solvent for polychlorinated arenes, and neat di-*n*-butyl ether works best for arenes having a preponderance of electron-withdrawing substituents. We have found that the more electron rich the arene, the more suitable it is for use in these student syntheses. Very electron-poor arenes (e.g., those having any NO_2 substituents or more than one other electron-withdrawing group) or those having bromo or iodo substituents are not suitable for this experiment. Most organic preparation rooms contain a variety of substituted anilines, anisole derivatives, and polyalkylated benzenes that are used as unknowns. These make excellent ligands for this reaction; however, the aniline derivatives generally react the most quickly (almost all going to completion in 3 to 20 hours) and give products that are the easiest to purify. We also find that using a small excess of $\text{Cr}(\text{CO})_6$ is preferable for most syntheses because it aids product purification. This is especially true for solid and high-boiling arenes. The use of a large excess of arene is preferable only for low-boiling, inexpensive, liquid arenes that are at least moderately electron rich. Buildup of $\text{Cr}(\text{CO})_6$ in the reflux condenser is a problem that can substantially complicate these syntheses. We find that the use of air-cooled reflux condensers for these reactions along with use of the THF cosolvent minimizes this problem. These reactions are easily scaled up or down to fit the availability of equipment and the preferences of the instructor. Thus, we have successfully

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¹Supplementary materials for this article are available in JCE Online at <http://jchemed.chem.wisc.edu/Journal/issues/1998/Jul/abs891.html>.

carried out many syntheses at multi-gram scales and have recently extended this work to microscales. The progress of these reactions can be monitored visually by color changes and by changes in the amount of white solid $\text{Cr}(\text{CO})_6$ sublimed into the condenser, but is best monitored by IR spectroscopy where one observes the appearance of carbonyl bands of the new products and eventually the loss of the band due to $\text{Cr}(\text{CO})_6$.

Characterization of the $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ Complexes and Their Properties

Compared to many other transition metal organometallics, these products are relatively stable in air. Thus, the yellow to orange powders or crystalline solids may be handled in air for short periods without the occurrence of noticeable decomposition. Powder samples are typically stable for at least several hours or days in air, while pure crystalline samples are often air stable for several years or more.² As expected, their solutions are more air sensitive, but most can be handled in air for short periods. In particular, they decompose sufficiently slowly that acceptable IR and NMR spectra can generally be successfully recorded in air. When they are heated in air as solids, these complexes rapidly decompose, but reversible melting points and/or sharp decomposition points are observed in sealed capillaries under dinitrogen.

The characterization of these materials by a combination of physical, spectroscopic, structural, and electrochemical methods forms a central part of this experiment. We have relied most heavily on analytical, IR, mass, and ^1H and ^{13}C NMR spectroscopic data to identify and characterize our products. In addition, we have employed single-crystal X-ray diffraction and cyclic voltammetric studies. A useful property of most of these complexes is that the arenes generally have relatively few types of protons, and these are observed over a wide range of chemical shifts. This, combined with the excellent solubilities of most of these complexes in CDCl_3 , means that the 60-MHz spectrometers commonly used in teaching labs are entirely adequate for the ^1H NMR studies. When developing their quantitative structure–property correlations (1, 7), we find it useful to have the students compare their data with those for the parent $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex, since this allows them to quickly evaluate substituent effects. Depending on the availability of other instrumentation in the lab and the instructor's interest, useful structure–property relationships should also be derivable from many other techniques commonly employed in the undergraduate lab curriculum. Examples that come to mind include UV–vis spectroscopy, powder X-ray diffraction, bomb calorimetry, polarography, and bulk electrolysis and thin-layer, gas, and high-performance liquid chromatography. In addition to having students compare one $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex to another, we also have them compare the properties of their products with those of the uncomplexed aromatic starting materials. This allows them to evaluate the effect of the $\text{Cr}(\text{CO})_3$ group on the aromatic ring, which is broadly similar to that of a nitro substituent.

Safety Precautions for These Studies

There are several potential safety hazards associated with these procedures. Like many metal carbonyls, $\text{Cr}(\text{CO})_6$ is a volatile toxic substance. Similarly, many aromatics are carcinogenic or otherwise toxic. Therefore, these reactions should

only be done in a well-ventilated fume hood while wearing gloves. Because of the high temperatures employed, only air-cooled condensers should be used for the conventional-scale syntheses. Occasionally when these reactions are overheated, insoluble green/gray residues (presumably finely divided metallic chromium metal) have formed, which have ignited paper towels and filter papers after the solvents have evaporated. To prevent this fire hazard, thoroughly wet any residues, filter papers, and paper towels used to clean the reaction flask with water before discarding them. Peroxides always present a potential hazard when organic solvents are used; take appropriate precautions. As in any synthesis involving air-sensitive compounds, pressurized inert gasses are used. Take appropriate precautions to prevent uncontrolled pressure buildups and violent glassware breakage.

Acknowledgments

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Supplementary Materials Online

Student materials, more detailed discussions of these issues to aid instructors, and experimental procedures are provided in *JCE Online* (<http://jchemed.chem.wisc.edu/Journal/issues/1998/Jul/abs891.html>). This material includes an introduction to the chemistry of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes suitable for inclusion in student handouts, suggestions for potential extensions to this work, more comprehensive safety suggestions, details of the reaction conditions as a function of arene, tips to ensure successful reactions, descriptions of the glassware used, generic reaction procedures, lists of required equipment, diagrams of assembled glassware, examples of both multi-gram-scale and microscale syntheses, and tabulations of characterization data for about five dozen $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ derivatives.

Notes

1. This excess $\text{Cr}(\text{CO})_6$ is easily and almost completely recovered in the reaction workup and can be reused.

2. This increased air sensitivity for powders compared to crystalline samples is common for organometallics and appears to be due to a combination of their greater surface area and larger number of crystalline defects.

Literature Cited

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Table I. IR, ¹³C NMR and Electrochemical Data for the Complexes

| <-----Arene Substituents-----> | <-----IR ^a -----> | <----- ¹³ C NMR ^b -----> (calculated) ppm | <--Electrochemical--> Data ^c |
|--------------------------------|------------------------------|--|--|
|--------------------------------|------------------------------|--|--|

| X1 | X2 | X3 | X4 | X5 | X6 | ν_{XO} A $\chi\mu-1$ | ν_{XO} E $\chi\mu-1$ | $\frac{-n1/2}{d}$ | KCOi x 105 dyne cm-1 | KCO x 105 dyne cm-1 | C1 | C2 | C3 | C4 | C5 | C6 | CO | E° (Ep,a) e V | E mV | ip,c/ip ,a |
|-------|-------|-----|----|----|----|--------------------------------|--------------------------------|-------------------|-------------------------------|------------------------------|-----------------------|-----------------------|-----------------------|-----------------|------------------|-----------------|------------|---------------------|---------|---------------|
| H | H | H | H | H | H | 1974 | 1894 | 2.4 | 0.42 | 14.90 | 95.15 | 95.15 | 95.15 | 95.15 | 95.15 | 95.15 | 234.0 | 0.877 | 84 | 0.91 |
| NEt2 | H | H | H | H | H | 1954 | 1864 | 2.5 | 0.46 | 14.49 | 135.9 | 74.72 | 99.30 | 82.83 | 99.30 | 74.72 | 235.7 | 0.582 | 133 | 0.87 |
| NMe2 | H | H | H | H | H | 1956 | 1868 | 2.7 | 0.45 | 14.54 | 136.1 | 76.17 | 98.82 | 84.14 | 98.82 | 76.17 | 235.5 | 0.577 | 73 | 0.89 |
| NH2 | H | H | H | H | H | 1962 | 1877 | 2.5 | 0.44 | 14.67 | 137.0 | 77.57 | 99.09 | 82.96 | 99.09 | 77.57 | 235.9 | 0.589 | 80 | 0.92 |
| OMe | H | H | H | H | H | 1973 | 1891 | 2.5 | 0.43 | 14.87 | 144.1 | 80.28 | 97.48 | 87.44 | 97.48 | 80.28 | 234.2 | 0.783 | 80 | 0.93 |
| F | H | H | H | H | H | 1982 | 1903 | 2.0 | 0.41 | 15.04 | 146.8 | 81.65 | 96.09 | 89.42 | 96.09 | 81.65 | 232.9 | 0.955 | 98 | 0.76 |
| Cl | H | H | H | H | H | 1986 | 1908 | 2.2 | 0.41 | 15.11 | 113.3 | 93.59 | 95.97 | 91.34 | 95.97 | 93.59 | 232.8 | 0.987 | 89 | 0.75 |
| Me | H | H | H | H | H | 1969 | 1889 | 2.2 | 0.42 | 14.83 | 111.7 | 96.62 | 94.79 | 91.85 | 94.79 | 96.62 | 234.2 | 0.846 | 88 | 0.92 |
| SiMe3 | H | H | H | H | H | 1968 | 1890 | 2.4 | 0.41 | 14.83 | 101.0 | 101.3 | 93.03 | 97.69 | 93.03 | 101.3 | 234.1 | 0.887 | 154 | 0.91 |
| CO2M | H | H | H | H | H | 1985 | 1911 | 2.3 | 0.39 | 15.14 | 91.05 | 96.04 | 92.47 | 97.46 | 92.47 | 96.04 | 231.9 | 1.027 | 81 | 0.78 |
| CF3 | H | H | H | H | H | 1990 | 1918 | 2.2 | 0.38 | 15.24 | 96.16 | 92.17 | 91.43 | 96.94 | 91.43 | 92.17 | 231.4 | 1.085 | 130 | 0.70 |
| OMe | OMe | H | H | H | H | 1965 | 1881 | 2.4 | 0.43 | 14.72 | 133.8 6 (129.4) | 133.8 6 (129.4) | 80.83 (82.7) | 89.19 (89.8) | 89.19 (89.8) | 80.83 (82.7) | 234.7 5 | 0.745 | 92 | 0.84 |
| NH2 | NH2 | H | H | H | H | 1954 | 1866 | 2.5 | 0.45 | 14.51 | 119.5 3 (119.6) | 119.5 3 (119.6) | 82.76 (81.6) | 87.86 (87.0) | 87.86 (87.0) | 82.76 (81.6) | 238.4 2 | 0.464 | 71 | 0.90 |
| F | Me | H | H | H | H | 1977 | 1898 | 2.3 | 0.41 | 14.96 | 144.7 4 (148.3) | 97.85 (98.2) | 96.98 (97.6) | 90.74 (89.1) | 94.10 (92.8) | 82.72 (81.3) | 233.2 6 | 0.913 | 113 | 0.89 |
| Me | Me | H | H | H | H | 1965 | 1883 | 2.8 | 0.42 | 14.74 | 109.8 2 (113.2) | 109.8 2 (113.2) | 97.13 (96.3) | 93.93 (91.5) | 93.43 (91.5) | 97.13 (96.3) | 234.6 9 | 0.808 | 100 | 0.87 |
| Me | CO2Me | H | H | H | H | 1980 | 1906 | 2.0 | 0.39 | 15.06 | 113.2 2 (112.6) | 92.33 (92.6) | 98.24 (95.7) | 90.50 (89.2) | 98.33 (97.2) | 94.71 (94.0) | 232.5 6 | 0.968 | 77 | 0.83 |
| NH2 | H | NH2 | H | H | H | 1952 | 1862 | 2.8 | 0.46 | 14.46 | 136.9 6 (141.4) | 67.87 (60.1) | 136.9 6 (141.4) | 69.94 (65.5) | 98.41 (103.1) | 69.94 (65.5) | 237.5 1 | 0.417 | 72 | 0.93 |
| OMe | H | OMe | H | H | H | 1965 | 1881 | 2.4 | 0.43 | 14.72 | 144.8 | 70.75 | 144.8 | 74.91 | 100.1 | 74.91 | 234.5 | 0.719 | 80 | 0.87 |

| | | | | | | | | | | | | | | | | | | | | |
|------|---|--------|------|---|---|------|------|-----|------|-------|-----------------------|------------------|-----------------------|-----------------------|------------------|-----------------|------------|-------|----|------|
| NH2 | H | OMe | H | H | H | 1958 | 1871 | 2.6 | 0.45 | 14.59 | 136.8 8 (139.5) | 68.62 (68.2) | 145.8 3 (148.2) | 70.71 (68.2) | 97.25 (101.5) | 73.28 (69.9) | 236.1 2 | 0.561 | 87 | 0.93 |
| NH2 | H | F | H | H | H | 1971 | 1889 | 2.4 | 0.43 | 14.84 | 135.4 2 (138.1) | 67.29 (64.1) | 150.5 1 (150.8) | 71.14 (69.5) | 98.88 (100.1) | 73.40 (71.9) | 235.1 8 | 0.675 | 78 | 0.82 |
| NH2 | H | Me | H | H | H | 1958 | 1874 | 2.5 | 0.43 | 14.62 | 136.8 9 (136.8) | 79.65 (79.1) | 113.7 2 (115.7) | 84.23 (84.5) | 96.68 (98.8) | 75.70 (74.3) | 236.1 2 | 0.567 | 86 | 0.95 |
| NH2 | H | C(O)Me | H | H | H | 1971 | 1893 | 2.7 | 0.41 | 14.88 | 136.6 9 (136.7) | 74.37 (77.1) | 102.4 7 (107.4) | 83.84 (82.5) | 98.31 (98.7) | 78.95 (81.9) | 235.2 8 | 0.714 | 66 | 0.89 |
| NH2 | H | CF3 | H | H | H | 1977 | 1900 | 2.4 | 0.40 | 14.98 | 136.0 4 (133.4) | 71.09 (74.7) | 102.2 4 (100.1) | 79.00 (80.1) | 97.65 (95.4) | 77.65 (79.4) | 234.2 3 | 0.755 | 78 | 0.95 |
| OMe | H | F | H | H | H | 1966 | 1888 | 2.4 | 0.40 | 14.80 | 146.3 6 (145.2) | 71.18 (66.8) | 149.9 0 (149.2) | 76.43 (73.9) | 96.20 (98.5) | 77.00 (74.6) | 234.6 0 | 0.867 | 88 | 0.71 |
| OMe | H | Me | H | H | H | 1966 | 1883 | 2.4 | 0.43 | 14.75 | 144.5 4 (143.9) | 82.00 (81.8) | 113.0 0 (114.1) | 88.44 (88.9) | 97.38 (97.2) | 78.08 (77.0) | 234.5 5 | 0.766 | 91 | 0.89 |
| OMe | H | CO2Me | H | H | H | 1979 | 1904 | 2.4 | 0.39 | 15.03 | 142.6 5 (141.6) | 78.76 (81.2) | 94.44 (93.5) | 88.23 (88.3) | 95.97 (94.9) | 82.35 (82.7) | 233.0 1 | 0.941 | 86 | 0.69 |
| F | H | Me | H | H | H | 1977 | 1900 | 2.1 | 0.40 | 14.98 | 145.7 6 (145.5) | 83.04 (83.10) | 112.1 9 (112.7) | 90.18 (90.9) | 95.98 (95.8) | 79.37 (78.3) | 233.3 5 | 0.936 | 69 | 0.62 |
| Cl | H | Me | H | H | H | 1977 | 1901 | 2.1 | 0.40 | 14.99 | 114.7 7 (113.1) | 93.96 (95.1) | 112.2 0 (112.6) | 91.50 (92.8) | 96.54 (95.7) | 90.91 (90.3) | 233.2 1 | 0.956 | 93 | 0.80 |
| Me | H | CO2Me | H | H | H | 1979 | 1906 | 2.3 | 0.38 | 15.05 | 109.6 1 (109.1) | 95.19 (97.5) | 92.86 (90.7) | 94.26 (92.7) | 93.13 (92.2) | 97.15 (99.0) | 232.6 7 | 0.993 | 68 | 0.82 |
| NH2 | H | Cl | H | H | H | 1969 | 1891 | 2.6 | 0.41 | 14.85 | 136.6 0 (138.0) | 77.91 (76.1) | 117.2 1 (117.4) | 83.19 (81.5) | 97.55 (100.0) | 75.05 (73.8) | 235.0 1 | 0.688 | 79 | 0.86 |
| NMe2 | H | H | NMe2 | H | H | 1946 | 1857 | 3.3 | 0.46 | 14.38 | 127.2 0 (125.2) | 79.55 (79.9) | 79.55 (79.9) | 127.2 0 (125.2) | 79.55 (79.9) | 79.55 (79.9) | 237.6 9 | 0.390 | 82 | 0.96 |
| NH2 | H | H | NH2 | H | H | 1954 | 1868 | 3.1 | 0.44 | 14.53 | 125.4 5 (125.0) | 80.86 (81.6) | 80.86 (81.6) | 125.4 5 (125.0) | 80.86 (81.6) | 80.86 (81.6) | 238.3 9 | 0.409 | 80 | 0.82 |
| OMe | H | H | OMe | H | H | 1966 | 1883 | 2.9 | 0.43 | 14.75 | 137.3 1 (82.7) | 81.69 (82.7) | 81.69 (82.7) | 137.3 1 (82.9) | 81.69 (82.9) | 81.69 (82.9) | 234.8 3 | 0.694 | 82 | 0.97 |

| | | | | | | | | | | | | | | | | | | | | |
|------|---|---|--------|---|---|------|------|-----|------|-------|-----------------------|-----------------|------------------|-----------------------|------------------|-----------------|------------|-------|-----|------|
| NMe2 | H | H | NH2 | H | H | 1949 | 1864 | 3.1 | 0.44 | 14.47 | 124.2 4 (124.1) | 78.44 (80.2) | 82.12 (81.3) | 129.0 4 (126.1) | 82.12 (81.3) | 78.44 (80.2) | 238.0 1 | 0.400 | 64 | 0.95 |
| NH2 | H | H | OMe | H | H | 1960 | 1870 | 2.8 | 0.46 | 14.59 | 131.1 5 (129.4) | 77.01 (80.0) | 85.21 (84.3) | 132.8 8 (132.1) | 85.21 (84.3) | 77.01 (80.0) | 236.6 1 | 0.535 | 68 | 0.92 |
| NH2 | H | H | F | H | H | 1970 | 1889 | 2.6 | 0.42 | 14.83 | 133.0 2 (131.4) | 75.03 (78.6) | 86.73 (85.6) | 136.5 6 (134.7) | 86.73 (85.6) | 75.03 (78.6) | 235.1 2 | 0.646 | 80 | 0.90 |
| NH2 | H | H | Cl | H | H | 1969 | 1888 | 2.7 | 0.42 | 14.82 | 135.1 1 (133.3) | 76.42 (78.5) | 98.38 (97.6) | 98.60 (101.3) | 98.38 (97.6) | 76.42 (78.5) | 234.7 3 | 0.660 | 97 | 0.86 |
| NMe2 | H | H | CO2Me | H | H | 1966 | 1886 | 2.3 | 0.41 | 14.78 | 137.8 4 (138.6) | 75.00 (73.6) | 98.75 (99.7) | 82.44 (80.1) | 98.75 (99.7) | 75.00 (73.6) | 233.1 7 | 0.721 | 74 | 0.89 |
| Me | H | H | CO2Me | H | H | 1981 | 1907 | 2.2 | 0.39 | 15.07 | 113.9 8 (114.1) | 92.74 (94.0) | 97.00 (95.7) | 88.64 (87.8) | 97.00 (95.7) | 92.74 (94.0) | 232.1 0 | 0.955 | 75 | 0.82 |
| NH2 | H | H | Me | H | H | 1958 | 1874 | 2.6 | 0.43 | 14.62 | 134.9 1 (133.8) | 77.77 (77.3) | 99.61 (100.6) | 97.97 (99.6) | 99.61 (100.6) | 77.77 (77.3) | 236.2 9 | 0.542 | 101 | 0.97 |
| NH2 | H | H | C(O)Me | H | H | 1971 | 1894 | 2.5 | 0.40 | 14.89 | 139.4 9 (141.4) | 76.67 (77.2) | 98.82 (98.8) | 89.41 (91.3) | 98.82 (98.8) | 76.67 (77.2) | 233.6 4 | 0.756 | 75 | 0.83 |
| NH2 | H | H | CO2Me | H | H | 1971 | 1894 | 2.4 | 0.40 | 14.89 | 139.2 1 (139.5) | 76.58 (75.0) | 99.22 (100.0) | 81.64 (79.0) | 99.22 (100.0) | 76.58 (75.0) | 233.6 5 | 0.730 | 70 | 0.84 |
| NH2 | H | H | CF3 | H | H | 1977 | 1898 | 2.3 | 0.41 | 14.96 | 138.7 5 (138.9) | 74.65 (73.5) | 95.61 (96.2) | 86.13 (84.0) | 95.61 (96.2) | 74.65 (73.9) | 233.3 3 | 0.779 | 87 | 0.84 |
| OMe | H | H | F | H | H | 1977 | 1898 | 2.8 | 0.41 | 14.96 | 139.0 2 (138.5) | 80.09 (81.3) | 83.99 (84.0) | 139.8 5 (139.1) | 83.99 (84.0) | 80.09 (81.3) | 233.3 9 | 0.841 | 87 | 0.89 |
| OMe | H | H | Me | H | H | 1966 | 1882 | 2.3 | 0.44 | 14.74 | 141.9 0 (140.9) | 80.95 (80.0) | 97.35 (99.0) | 103.3 8 (104.0) | 97.35 (99.0) | 80.95 (80.0) | 234.5 6 | 0.745 | 115 | 0.99 |
| OMe | H | H | CO2Me | H | H | 1980 | 1905 | 2.2 | 0.39 | 15.05 | 145.6 1 (145.6) | 78.98 (77.7) | 97.32 (98.4) | 85.35 (83.4) | 97.32 (98.4) | 78.98 (77.7) | 231.8 8 | 0.941 | 89 | 0.82 |
| F | H | H | Me | H | H | 1977 | 1899 | 2.3 | 0.41 | 14.97 | 144.6 8 (143.5) | 82.59 (81.3) | 95.79 (97.6) | 105.9 1 (106.0) | 95.79 (97.6) | 82.59 (81.3) | 233.2 6 | 0.910 | 87 | 0.89 |
| Cl | H | H | Me | H | H | 1977 | 1902 | 2.2 | 0.39 | 15.00 | 109.6 4 (109.3) | 94.88 (93.3) | 95.46 (97.5) | 108.2 8 (107.5) | 95.46 (97.5) | 94.88 (93.3) | 233.0 6 | 0.930 | 84 | 0.91 |

| | | | | | | | | | | | | | | | | | | | | |
|-----------------|-----|--------------------|----|--------------------|----|------|------|-----|------|-------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------|-------|----|------|
| NH ₂ | H | CO ₂ Me | H | CO ₂ Me | H | 1981 | 1909 | 2.6 | 0.38 | 15.09 | 130.6 4 (131.9) | 76.45 (80.9) | 95.65 (92.5) | - (84.8) | 95.65 (92.5) | 76.45 (80.9) | 234.0 0 | 0.832 | 73 | 0.87 |
| Me | Me | H | Me | H | H | 1961 | 1880 | 2.5 | 0.42 | 14.69 | 110.1 2 (109.9) | 110.8 5 (112.9) | 98.30 (97.8) | 106.5 5 (108.1) | 93.48 (93.0) | 97.27 (96.0) | 234.9 4 | 0.764 | 91 | 0.96 |
| OMe | OMe | OMe | H | H | H | 1963 | 1879 | 2.4 | 0.43 | 14.69 | 140.7 0 (131.8) | 121.5 7 (114.6) | 140.7 0 (131.8) | 71.71 (75.0) | 91.89 (92.2) | 71.21 (75.0) | 234.7 9 | 0.704 | 94 | 0.80 |
| Me | Me | H | Me | Me | H | 1957 | 1871 | 2.4 | 0.44 | 14.58 | 108.0 8 (109.6) | 108.0 8 (109.6) | 99.34 (97.5) | 108.0 8 (109.6) | 108.0 8 (109.6) | 99.34 (97.5) | 235.3 3 | 0.774 | 75 | 0.97 |
| Me | Me | Me | Me | Me | H | 1952 | 1868 | 2.3 | 0.43 | 14.52 | 106.7 4 (109.3) | 108.8 4 (111.1) | 110.3 0 (114.1) | 108.8 4 (111.1) | 106.7 4 (109.3) | 97.11 (94.2) | 235.5 8 | 0.709 | 82 | 0.92 |
| Me | Me | Me | Me | Me | Me | 1948 | 1864 | 2.4 | 0.43 | 14.46 | 107.6 3 (110.8) | 107.6 3 (110.8) | 107.6 3 (110.8) | 107.6 3 (110.8) | 107.6 3 (110.8) | 107.6 3 (110.8) | 235.9 0 | 0.668 | 82 | 0.92 |

a Recorded in CH₂Cl₂.

b Recorded in (CD₃)₂SO.

c Electrochemical data recorded in CH₂Cl₂ (0.1 M in [*n*-Bu₄N]PF₆) at a Pt-bend electrode and at a scan rate of 100 mVs⁻¹. Potentials are reported *versus* SCE.

d E band width at half height divided by A₁ band width at half height.

e For chemically irreversible oxidations, E_{p,a} is reported in brackets (recorded at 0.1 Vs⁻¹).

Table II. ^1H NMR Data for the Arenes and their Substituents and ^{13}C NMR Data for the Arene Substituents of the $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ Complexes $(\text{CD}_3)_2\text{SO}$.

| | | 13C NMR b of | |
|----------------|--|-------------------------------------|-----------------------------------|
| | 1H NMR b | | |
| Arene | Arenes ppm (Hz) | Substituents ppm (Hz) | Substituents ppm |
| C6H6 | 5.68 (s, 6H) | - | - |
| C6H5NMe2 | 5.88 (d, 2H, J=7) 5.19 (d, 2H, J=7) 5.11 (t, 1H, J=7) | 2.84 (s, 6H) | 39.24 |
| C6H5NEt2 | 5.87 (t, 2H, J=7) 5.13 (d, 2H, J=7) 5.01 (t, 1H, J=7) | 3.22 (q, 4H, J=7) 1.09 (t, 6H, J=7) | 43.32 (CH2CH3) 11.71 (CH2CH3) |
| C6H5NH2 | 5.81 (t, 2H, J=6.5) 5.03 (d, 2H, J=6.5) 4.93 (t, 1H, J=6.5) | 5.89 (s, 2H) | - |
| C6H5OMe | 5.93 (t, 2H, J=7) 5.56 (d, 2H, J=7) 5.21 (t, 1H, J=7) | 3.68 (s, 3H) | 55.78 |
| C6H5F | 5.97 (s, 2H) 5.95 (s, 2H) 5.27 (s, 1H) | - | - |
| C6H5Cl | 5.97 (d, 2H) 5.90 (t, 2H) 5.47 (t, 1H) | - | - |
| C6H5Me | 5.79 (t, 2H, J=6.5) 5.57 (d, 2H, J=6.5) 5.48 (t, 1H, J=6.5) | 2.13 (s, 3H) | 20.14 |
| C6H5SiMe3 | 5.90 (t, 1H, J=6.5) 5.79 (d, 2H, J=6.5) 5.54 (t, 2H, J=6.5) | 0.26 (s, 9H) | -1.49 (Si(CH3)3) |
| C6H5CO2Me | 5.43 (d, 2H, J=6.5) 5.16 (t, 1H, J=6.5) 4.87 (t, 2H, J=6.5) | 3.83 (s, 3H) | 165.33 (CO2CH3) 52.80 (CO2CH3) |
| C6H5CF3 | 6.24 (d, 2H, J=6.5) 5.99 (t, 1H, J=6.5) 5.75 (t, 2H, J=6.5) | - | 123.17 |
| 1,2-C6H4FMe | 6.07 (t, 1H, J=6) 5.97 (t, 1H, J=6) 5.78 (s, 1H) 5.40 (t, 1H, J=6) | 2.18 (s, 3H) | 14.043 |
| 1,2-C6H4(NH2)2 | 5.41 (s, 2H) 5.10 (s, 2H) | 5.29 (s, 2H) | - |
| 1,2-C6H4Me2 | 5.74 (dd, 2H) 5.59 (dd, 2H) | 2.13 (s, 6H) | 18.304 |
| 1,2-C6H4(OMe)2 | 5.92 (dd, 2H, J=5, J=3) 5.44 (dd, 2H, J=5, J=3) | 3.71 (s, 6H) | 56.738 |

| | | | |
|---|---|--|--|
| 1,2-C ₆ H ₄ (CO ₂ Me)(Me) | 6.34 (d, 1H, J=6) 6.05 (t, 1H, J=6) 5.59 (d, 1H, J=6) 5.58 (t, 1H, J=6) | 2.43 (s, 3H) 3.82 (s, 3H) | 165.96 (CO ₂ CH ₃) 52.86 (CO ₂ CH ₃) 20.50 (CH ₃) |
| 1,3-C ₆ H ₄ (NH ₂) ₂ | 5.69 (t, 1H, J=6.5) 4.84 (t, 1H, J=2.0) 4.53 (dd, 2H, J=6.5, J=2.0) | 5.59 (s, 4H) | - |
| 1,3-C ₆ H ₄ (OMe) ₂ | 6.02 (t, 1H, J=7) 5.68 (t, 1H, J=2) 5.29 (dd, 2H, J=7, J=2) | 3.70 (s, 6H) | 56.03 |
| 1,3-C ₆ H ₄ Cl ₂ | 6.52 (s, 1H) 6.09 (t, 1H) 5.85 (d, 2H) | - | - |
| 1,3-C ₆ H ₄ Me ₂ | 5.83 (t, 1H, J=6.5) 5.48 (s, 1H) 5.39 (d, 2H, J=6.5) | 2.13 (s, 6H) | 20.05 |
| 1,3-C ₆ H ₄ (CO ₂ Me) ₂ | 6.71 (s, 1H) 6.58 (d, 2H) 5.78 (t, 1H) | 3.86 (s, 3H) | 164.56 (CO ₂ CH ₃) 53.11 (CO ₂ CH ₃) |
| 1,3-C ₆ H ₄ (NH ₂)(OMe) | - | - | 55.37 |
| 1,3-C ₆ H ₄ Cl(NH ₂) | 5.90 (s, 1H) 5.33 (s, 2H) 4.88 (s, 1H) | 6.14 (s, 2H) | - |
| 1,3-C ₆ H ₄ Me(NH ₂) | 5.86 (s, 1H) 4.96 (s, 1H) 4.88 (s, 2H) | 5.86 (s, 2H) 2.10 (s, 3H) | 20.71 |
| 1,3-C ₆ H ₄ (COMe)(NH ₂) | 5.98 (t, 1H, J=6.5) 5.57 (d, 1H, J=6.5) 5.44 (s, 1H) 5.26 (d, 1H, J=6.5) | 6.18 (s, 2H) 2.40 (s, 3H) | 198.34 (CO ₂ CH ₃) 25.53 (CO ₂ CH ₃) |
| 1,3-C ₆ H ₄ F(OMe) | 6.20 (d, 1H, J=5) 6.08 (d, 1H, J=5) 5.59 (t, 1H, J=5) 5.36 (t, 1H, J=5) | 3.75 (s, 3H) | 56.47 |
| 1,3-C ₆ H ₄ (OMe)Me | 5.95 (t, 1H, J=6.5) 5.59 (q, 1H, J=1) 5.46 (dm, 1H, J=6.5) 5.17 (d, 1H, J=6.5) | 3.71 (s, 3H, OCH ₃) 2.20 (s, 3H, CH ₃) | 55.77 (OCH ₃) 20.19 (CH ₃) |
| 1,3-C ₆ H ₄ (OMe)(CO ₂ Me) | 6.06 (t, 1H, J=6.5) 5.83 (s, 1H) 5.82 (d, 1H, J=6.5) 5.76 (d, 1H, J=6.5) | 3.87 (s, 3H) 3.74 (s, 3H) | 166.29 (CO ₂ CH ₃) 56.28 (OCH ₃) 52.99 (CO ₂ CH ₃) |
| 1,3-C ₆ H ₄ FMe | 6.02 (m, 1H) 6.00 (s, 1H) 5.89 (m, 1H) 5.28 (d, 1H, J=6) | 2.26 (s, 3H) | 19.72 |
| 1,3-C ₆ H ₄ ClMe | 5.97 (t, 1H, J=6.5) 5.97 (s, 1H) 5.84 (dq, 1H, J _d =6.5, J _q =0.75) 5.39 (d, 1H, J=6.5) | 2.20 (s, 3H) | 19.69 |

| | | | |
|----------------------|--|---|--|
| 1,3-C6H4(CO2Me)Me | 6.18 (s, 1H) 6.08 (d, 1H, J=6) 5.90 (t, 1H, J=6) 5.86 (d, 1H, J=6) | 3.85 (s, 3H, CO2CH3) 2.19 (s, 3H, CH3) | 165.82 (CO2CH3) 52.86 (CO2CH3) 19.86 (CH3) |
| 1,4-C6H4(NMe2)2 | 5.28 (s, 4H) | 2.70 (s, 12H) | <i>b</i> |
| 1,4-C6H4(NH2)2 | 5.18 (s, 4H) | 4.9 (s, 4H) | - |
| 1,4-C6H4(OMe)2 | 5.76 (s, 4H) | 3.61 (s, 6H) | 56.45 |
| 1,4-C6H4Cl2 | 6.21 (s, 4H) | - | - |
| 1,4-C6H4Me2 | 5.65 (s, 4H) | 2.05 (s, 6H) | 19.62 |
| 1,4-C6H4(CO2Me)2 | 6.30 (s, 4H) | 3.87 (s, 6H) | 165.20 (CO2CH3) 52.12 (CO2CH3) |
| 1,4-C6H4(NMe2)(NH2) | 5.38 (d, 2H, J=6) 5.08 (d, 2H, J=6) | 5.28 (s, 2H) 2.58 (s, 6H) | <i>b</i> |
| 1,4-C6H4(OMe)(NH2) | 5.77 (d, 2H, J=7.5) 5.09 (d, 2H, J=7.5) | 5.50 (s, 2H) 3.52 (s, 3H) | 56.376 |
| 1,4-C6H4F(NH2) | 6.18 (dd, 2H, J=7.5, J=5.0) 5.05 (dd, 2H, J=7.5, J=2.5) | 5.77 (s, 3H) | - |
| 1,4-C6H4Cl(NH2) | 6.15 (d, 2H, J=7) 5.06 (d, 2H, J=7) | 5.97 (s, 2H) | - |
| 1,4-C6H4(NH2)Me | 5.77 (d, 2H, J=6.5) 5.04 (d, 2H, J=6.5) | 5.70 (s, 2H) 1.94 (s, 3H) | 19.38 |
| 1,4-C6H4(NH2)(COMe) | 6.45 (s, 2H) 5.13 (d, 2H, J=6) | 6.45 (s, 2H) 2.35 (s, 3H) | 194 (C(O)CH3) 25.07 (C(O)CH3) |
| 1,4-C6H4(NH2)(CO2Me) | 6.38 (d, 2H, J=8) 5.10 (d, 2H, J=8) | 6.40 (s, 2H) 3.73 (s, 3H) | 165.84 (CO2CH3) 51.25 (CO2CH3) |
| 1,4-C6H4(NH2)CF3 | 6.26 (d, 2H, J=7.5) 5.05 (d, 2H, J=7.5) | 6.40 (s, 2H) | 123.82 |
| 1,4-C6H4F(OMe) | 6.25 (t, 2H, J=5.0) 5.77 (d, 2H, J=5.0) | 3.61 (s, 3H) | 56.66 |
| 1,4-C6H4(OMe)Me | 5.84 (d, 2H, J=7.5) 5.60 (d, 2H, J=7.5) | 3.64 (s, 3H, OCH3) 2.04 (s, 3 H, CH3) | 55.88 (OCH3) 19.11 (CH3) |
| 1,4-C6H4(OMe(CO2Me)) | 6.46 (d, 2H, J=7) 5.67 (d, 2H, J=7) | 3.80 (s, 3H) 3.75 (s, 3H) | 164.6 (CO2CH3) 55.43 (OCH3) 51.71 (CO2CH3) |
| 1,4-C6H4FMe | 6.02 (t, 2H, J=6) 5.87 (m, 2H) | 2.03 (s, 3H) | 19.10 |
| 1,4-C6H4ClMe | 6.09 (d, 2H, J=7.0) 5.79 (d, 2H, J=7.0) | 2.06 (s, 3H) | 19.30 |

| | | | |
|--|---|--|---|
| 1,4-C ₆ H ₄ (NMe ₂)(CO ₂ Me) | 6.40 (d, 2H, J=7) 5.30 (d, 2H, J=7) | 3.78 (s, 3H) 2.91 (s, 6H) | ^b 165.523 (CO ₂ CH ₃) 51.191 (CO ₂ CH ₃) |
| 1,4-C ₆ H ₄ (CO ₂ Me)Me | 6.38 (d, 2H, J=6) 5.62 (d, 2H, J=6) | 3.82 (s, 3H, OCH ₃) 2.24 (s, 3H, CH ₃) | 165.16 (CO ₂ CH ₃) 52.74 (CO ₂ CH ₃) 20.00 (CH ₃) |
| 1,4-C ₆ H ₄ (NH ₂)But | 5.95 (d, 2H, J=7) 4.95 (d, 2H, J=7) | 5.84 (s, 2H) 1.17 (s, 9H) | 32.96 (C(CH ₃) ₃) 30.97 (C(CH ₃) ₃) |
| 1,3,5-C ₆ H ₃ (OMe) ₃ | 5.47 (s, 3H) | 3.25 (s, 9H) | 56.24 |
| 1,3,5-C ₆ H ₃ Me ₃ | 5.35 (s, 3H) | 2.14 (s, 9H) | 19.97 |
| 1,3,5-C ₆ H ₃ (CO ₂ Me) ₃ | 6.88 | 3.90 | 163.85(CO ₂ CH ₃) 52.47(CO ₂ CH ₃) |
| 1,2,3-C ₆ H ₃ (OMe) ₃ | 5.87 (t, 1H, J=7) 5.38 (d, 2H, J=7) | 3.79 (s, 6H) 3.74 (s, 3H) | 64.972 (?) 56.535 |
| 1,2,4,5-C ₆ H ₂ Me ₄ | 5.77 (s, 2H) | 2.08 (s, 12H) | 17.76 |
| 1,2,3,4,5-C ₆ HMe ₅ | 5.62 (s, 1H) | 2.23 (s, 3H) 2.15 (s, 6H) 2.11 (s, 6H) | 19.32 16.70 15.45 |
| C ₆ Me ₆ | - | 2.20 (s) | 16.73 |
| 1,3,4-C ₆ H ₃ Me ₃ | 5.82 (d, 1H, J=6.5) 5.63 (s, 1H) 5.48 (d, 1H, J=6.5) | 2.15 (s, 3H) 2.08 (s, 3H) 2.06 (s, 3H) | 19.56 18.26 17.81 |
| 1,3,5-C ₆ H ₃ (NH ₂)(CO ₂ Me) | 7.64 (s, 1H) 7.41 (s, 2H) | 5.74 (s, 2H) 3.83 (s, 6H) | 165.949 (CO ₂ CH ₃) 52.004 (CO ₂ CH ₃) |

^a ¹H and ¹³C NMR spectra were measured at 300.135 MHz and 75.469 MHz, respectively.

^b These signals for the N(CH₃)₂ carbon atoms were obscured by the (CD₃)₂SO resonance at 39.50 ppm.

**Synthesis and Structure/Property Relationships in (η^6 -Arene)Cr(CO)₃ Chemistry:
from Guided Experiments to Discovery Research.
Physical Properties, IR, MS, and Multinuclear NMR Spectra, and Cyclic
Voltammetry.**

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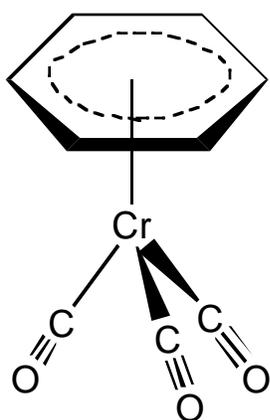
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Background and rationale. An emerging trend in the design of new laboratory experiments is to choose ones that provide a student experience that as closely as possible duplicates the research experience. One approach to making this experience more authentic is to ensure that no two students in a class and ideally, no two classes over a student generation (i.e. several years) prepare the same product. A series of target molecules having the same basic structure but different substituents is ideal for these purposes. Unfortunately, each additional reagent purchased to give the students variety also rapidly increases total lab costs. Thus, as many of the reagents as possible for any new discovery research project should already be available in the departmental chemical inventory. Since any instructor's time to validate new experimental procedures is limited, the series of target syntheses should all have closely related reaction conditions, and the factors that effect reaction conditions, yield, and product purification and identification should be well understood. Experience has also shown that students tend to have more confidence and learn more from each other if teams of students or the whole class work on related reactions at the same time. Unfortunately, this is difficult if expensive specialized glassware and equipment is required. An additional benefit of having each student prepare a different, but related derivative is that the students can be asked to compare their results and develop structure/property correlations.



$(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ complexes have been extensively described in the literature (1, 2) and are discussed in most courses dealing with transition metal organometallic chemistry. This interest arises both from both the fascinating theoretical, spectroscopic, structural, and reactivity properties of these molecules and their application to applied areas as varied as transition metals in organic synthesis and organometallic polymer chemistry (1, 2). They would seem to be ideal candidates for the inorganic or organic synthesis lab since they are relatively simple and inexpensive to prepare; they are only moderately air sensitive; and they can be prepared for a wide range of arenes (1). Indeed, a congeneric complex, $(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)\text{Mo}(\text{CO})_3$, has been a standard in the inorganic lab for several decades (3, 4). In spite of these facts, the chromium complexes have not been as widely utilized in teaching labs as they could be. In this paper, we suggest the use of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes in the inorganic laboratory for guided experiments, discovery research/cooperative learning labs (5), and special projects .

Syntheses of the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes. $(\eta^6\text{-Arene})\text{Cr}(\text{CO})_3$ complexes have been prepared by a wide variety of methods. In our hands, the simplest and most general is the thermal reaction of $\text{Cr}(\text{CO})_6$ and the arene of choice in an ether solvent, i.e.



For arenes that are relatively electron rich and having a predominance of R, OR, and NR_2 (where R = H, alkyl, or aryl) substituents but no more than one electron withdrawing halogen, CO_2R , or CF_3 substituent, these reactions are generally very clean and proceed to completion in from about three hours to about three days. Indeed, overnight reaction times are almost always sufficient for the aniline derivatives, especially when an two to four fold excess of $\text{Cr}(\text{CO})_6$ is employed.¹ For most arenes, such syntheses are best carried out in a 9:1 mixture of di-*n*-butyl ether and tetrahydrofuran (1a, 6). For

¹ This excess $\text{Cr}(\text{CO})_6$ is easily and almost completely recovered in the reaction workup and can be reused.

electron poor arenes, the reaction times are longer (typically several days to a week) and ideal reaction conditions are more varied. However, generally dioxane appears to be the best solvent for poly-chlorinated arenes, and neat di-n-butyl ether works best for arenes having a preponderance of electron withdrawing substituents. We have found that the more electron rich the arene, the more suitable it is for use in these student syntheses. Very electron poor arenes (e.g. those having any NO₂ substituents or more than one other electron withdrawing group) or those having bromo or iodo substituents are not suitable for this experiment. Most organic preparation rooms contain a variety of substituted anilines, anisole derivatives, and polyalkylated benzenes which are used as unknowns. These all make excellent ligands for this reaction; however, the aniline derivatives generally react the most quickly (i.e. almost all going to completion in 3 to 20 hours) and give products that are the easiest to purify. We also find that using a small excess of Cr(CO)₆ is preferable for most syntheses because it aids product purification. This is especially true for solid and high boiling arenes. The use of a large excess of arene is preferable only for low boiling, inexpensive, liquid arenes that are at least moderately electron rich. Buildup of Cr(CO)₆ in the reflux condenser is a problem which can substantially complicate these syntheses. We find that the use of air cooled reflux condensers for these reactions along with the use of the THF co-solvent largely prevents this problem. These reactions are easily scaled up or down to fit the availability of equipment and the preferences of the instructor. Thus, we have successfully carried many syntheses out at multi-gram scales and have recently extended this work to microscales. The progress of these reactions can be monitored visually by color changes and by changes in the amount of white solid Cr(CO)₆ sublimed into the condenser but is best monitored by IR spectroscopy where one observes the carbonyl bands of the new products growing in and eventually the loss of the band due to Cr(CO)₆.

Characterization of the (η^6 -arene)Cr(CO)₃ complexes and their properties.

Compared to many other transition metal organometallics, these products are relatively stable in air. Thus, the yellow to orange powders or crystalline solids may be handled in air for short periods of time without the occurrence of noticeable decomposition. Powder samples are typically stable for

at least several hours or days in air while pure crystalline samples are often air stable for several years or more.² As expected, their solutions are more air sensitive, but most can be handled in air for short periods of time. In particular, they decompose sufficiently slowly that acceptable IR and NMR spectra can generally be successfully recorded in air. When they are heated in air as solids, these complexes rapidly decompose, but reversible melting points and/or sharp decomposition points are observed in sealed capillaries under dinitrogen.

The characterization of these materials by a combination of physical, spectroscopic, structural, and electrochemical methods forms a central part of this experiment. We have relied most heavily on analytical, IR, mass, and ^1H and ^{13}C NMR spectroscopic data to identify and characterize our products. In addition, we have also employed single crystal X-ray diffraction and cyclic voltammetric studies. A useful property of these complexes is that the arenes generally have relatively few types of protons, and these are observed over a wide range of chemical shifts. This, combined with the excellent solubilities of these complexes in CDCl_3 , means that the 60 MHz spectrometers commonly used in teaching labs are entirely adequate for the ^1H NMR studies. When developing their quantitative structure/property correlations (1, 7), we find it useful to have the students compare their data to that for the parent $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex since this allows them to quickly evaluate substituent effects. Depending on the availability of other instrumentation in the lab and the instructor's interest, useful structure property relationships should also be derivable from many other techniques commonly employed in the undergraduate lab curriculum. Examples which come to mind include: UV-Visible spectroscopy, powder X-ray diffraction, bomb calorimetry, polarography and bulk electrolysis, thin layer, gas, and high performance liquid chromatography. In addition to having students compare one $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex to another, we also have them compare the properties of their products to those of the uncomplexed aromatic starting materials. This allows them to evaluate the effect of the $\text{Cr}(\text{CO})_3$ group on the

² This increased air sensitivity for powders compared to crystalline samples is common for organometallics and appears to be due to a combination of the great surface area and larger number of crystalline defects found for powders as well as the lower purity often associated with powders.

aromatic ring, which is broadly similar to that of a nitro substituent.

Safety precautions for these studies. There are several potential safety hazards associated with these procedures. Like many metal carbonyls, $\text{Cr}(\text{CO})_6$ is a volatile toxic substance. Similarly, many aromatics are carcinogenic and/or are otherwise toxic. Therefore, these reactions should only be handled while wearing gloves in a well ventilated fume hood. Because of the high temperatures employed, only air cooled condensers should be used for the conventional scale syntheses. Occasionally when these reactions are overheated, insoluble green/gray residues (presumably finely divided metallic chromium metal) have formed which have ignited paper towels and filter papers after the solvents have evaporated. To prevent this potential fire hazard, thoroughly wet any residues, filter papers, and paper towels used to clean the reaction flask with water before discarding them. Peroxides always present a potential hazard when dealing with organic solvents, take appropriate precautions. As with any synthesis involving air sensitive compounds, pressurized inert gasses are used. Take appropriate precautions to prevent uncontrolled pressure buildups and violent glassware breakage.

Contents of the WEB Version of this Article. More detailed discussions of these issues to aid instructors, student materials, and experimental procedures are available in the WEB version of *this Journal* (57 pages in total). Included are an introduction to the chemistry of (η^6 -arene)Cr(CO)₃ complexes suitable for inclusion in student handouts, suggestions for potential extensions to this work, more detailed safety suggestions, details of the reaction conditions as a function of arene, tips to ensure successful reactions, descriptions of the glassware used, generic reaction procedures, lists of required equipment, diagrams of assembled glassware, examples of both multi-gram scale and microscale syntheses, and tabulations of characterization data for about *five dozen* (η^6 -arene)Cr(CO)₃ derivatives.

Acknowledgments: The authors would like to acknowledge the generous support of the National Science Foundation, the Ohio Board of Regents, and Youngstown State University for grants used to fund this work. Funding was provided for instrumentation facilities used by the students carrying out this work, including the following: the NMR spectrometer (1996 OBoR (Ohio Board of Regents) Investment Fund grant: Ohio NMR Consortium "An Outstanding Opportunity for Ohio" #CAP-419), the GCQ mass spectrometer (NSF-ILI-IP grant DUE-9551683), and the X-ray diffractometers (NSF-RUI grant DUE-9403889, 1994 OBoR Action Fund grant #CAP-098, and a 1995 OBoR Investment Fund grant: "Ohio Crystallography Consortium at Toledo" CAP-075). L. J. B., S. J. D., and D. L. B. would like to thank Youngstown State University for teaching assistantships and summer support. A. D. H. would like to thank Youngstown State University for Research Professorships (for 1993/94 and 1994/95), a Faculty Improvement Leave (1995/96), Faculty Development Time (1994/1995 and 1996/97), and University Research Grants (grant #854 and #883), parts of which were used to develop this laboratory project.

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WEB Supplement for:

**Synthesis and Structure/Property Relationships in (η^6 -Arene)Cr(CO)₃ Chemistry:
from Guided Experiments to Discovery Research.
Physical Properties, IR, MS, and Multinuclear NMR Spectra, and Cyclic
Voltammetry.**

Allen D. Hunter,* Larry J. Bianconi, Steven J. DiMuzio, and Dianne L. Braho

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Abstract (1 page)

Background Discussion on (η^6 -Arene)Cr(CO)₃ Chemistry Suitable for Student Use (24 pages)

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Abstract of the Paper for the WEB version of *this Journal*

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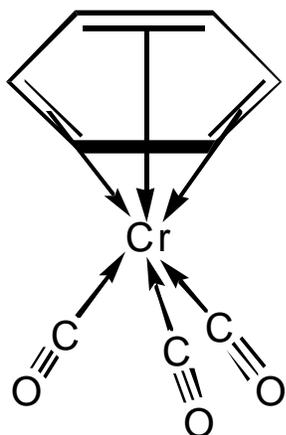
(η^6 -Arene)Cr(CO)₃ complexes are only moderately air sensitive and can easily and inexpensively be prepared from most of the arenes already found in organic stockrooms. Since instructors can have each student prepare a different complex, they are ideal targets for student directed “discovery research” lab projects. Teams of students can compare how their syntheses and the physical, spectroscopic, and electrochemical properties of their products vary as a function of the arenes’ structures. The resulting empirical structure/property correlations can then be rationalized in terms of various bonding models. A discussion of (η^6 -arene)Cr(CO)₃ chemistry suitable for student handouts is included along with suggestions for extending this experiment to create multi-step organic and inorganic synthesis projects. In addition, generic procedures for the syntheses using relatively simple glassware, example reaction procedures at both micro and conventional scales, practical hints for carrying out the syntheses, a discussion of substituent effects on arene suitability, lists of required equipment, and diagrams of the assembled glassware are included. Characterization data for over *five dozen* (η^6 -arene)Cr(CO)₃ complexes are tabulated. These data are particularly suitable for use as lecture, examination, and/or problem set examples in discussions of the relationships between structure, bonding, spectroscopy, electrochemistry, and reactivity in organometallic chemistry.

Background Discussion on (η^6 -Arene)Cr(CO)₃ Chemistry Suitable for Student Use

General background information on structures and bonding in (η^6 -arene)Cr(CO)₃ complexes. Organometallic complexes have been prepared for all of the transition metals and for a large variety of ligands (1-7). For “well behaved” organometallics (e.g. those of the mid-transition series in low oxidation states), the metal-ligand interactions can be understood in terms of several elementary approaches, including the following: Lewis acid-base interactions, the eighteen electron rule, valence bond theory, and localized molecular orbital approaches (e.g. the Dewar/Chatt/Duncanson model). Each of these models has advantages and disadvantages as tools for rationalizing aspects of the observed structures and properties. Even though these pictures are not as “rigorously correct” as the results of full molecular orbital analyses, their simplicity and surprisingly good explanatory powers means that they are still the most widely employed bonding descriptions used by practicing organometallic chemists.

The structures of organometallics have been established by a variety of different techniques ranging from elementary isomer number ideas through indirect spectroscopic means to direct methods such as X-ray crystallography. It is to these experimental three-dimensional structures that one tries to fit a bonding model. Remember, it is the observed numbers of ligands, bond angles, bond lengths, spectra, etc., which remain constant while we jump back and forth between different bonding pictures trying to find a satisfactory answer to our questions.

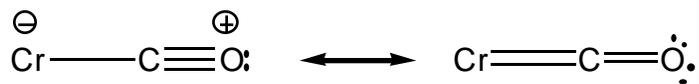
The most elementary bonding model is derived from Lewis acid-base theory. In this model, the metal-ligand bond is considered to arise from dative interactions between pair(s) of electrons on the ligand(s) and Lewis acid sites on the central metal atom. In terms of this model, the (η^6 -arene)Cr(CO)₃ complex has six such dative interactions. The first three take the form of single lone pairs being donated from the carbon atoms of the carbonyl ligands to chromium. The final three take the form of the three pairs of electrons in the three π -bonds of the arene being donated to chromium.



The eighteen electron rule is an empirical observation that states that complexes of the mid-transition elements in low formal oxidation states will be most stable when they have a total of eighteen valence electrons associated with the central metal atom. This empirical rule is related to the fact that such organometallics have a stable closed shell noble gas configuration. An η^6 -bonded arene can donate a total of six electrons to chromium while each carbonyl can donate two. Since this chromium atom is in the neutral oxidation state, it is said to have a d^6 configuration and is, therefore, said to contribute six electrons to the electron count. Thus, the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex has an eighteen electron configuration ($6 + 3(2) + 6 = 18$) and is expected to be relatively stable.

The bonding between the carbonyl ligands and the chromium center can better be described in terms of complementary valence bond and molecular orbital bonding models. In the valence

bond model, the metal-carbonyl interaction is explained in terms of two resonance forms, i.e.



Resonance Form I

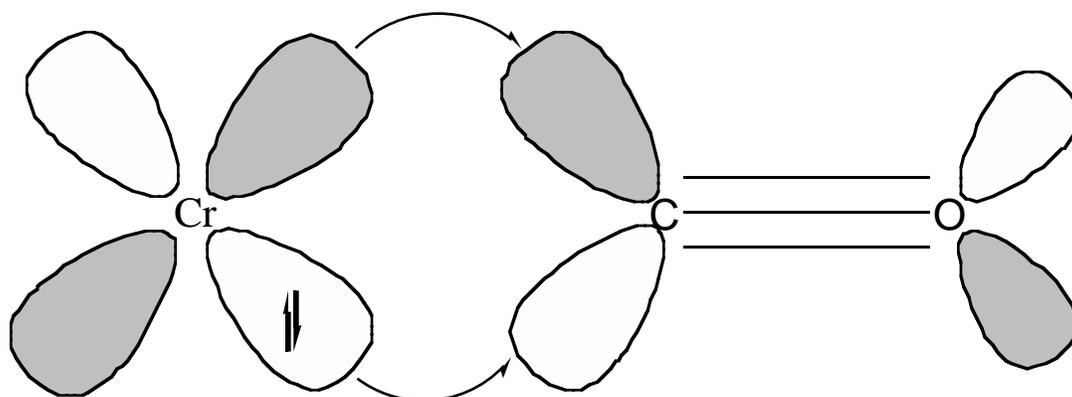
Resonance Form II

With electron rich metal centers, the second resonance form predominates, and the observed Cr-C bond order is relatively high (i.e. approaching two), and the C-O bond order is relatively low (i.e. approaching two) corresponding to relatively short Cr-C bonds and long C-O bonds. With electron poor metal centers, the first resonance form predominates, and the observed Cr-C bond order is relatively low (i.e. nearer to one), and the C-O bond order is relatively high (i.e. nearer to three) corresponding to relatively long Cr-C bonds and short C-O bonds.

From a molecular orbital perspective, this chromium-carbonyl interaction is explained as having two components, i.e.



σ -Symmetry Interaction: σ -Donation

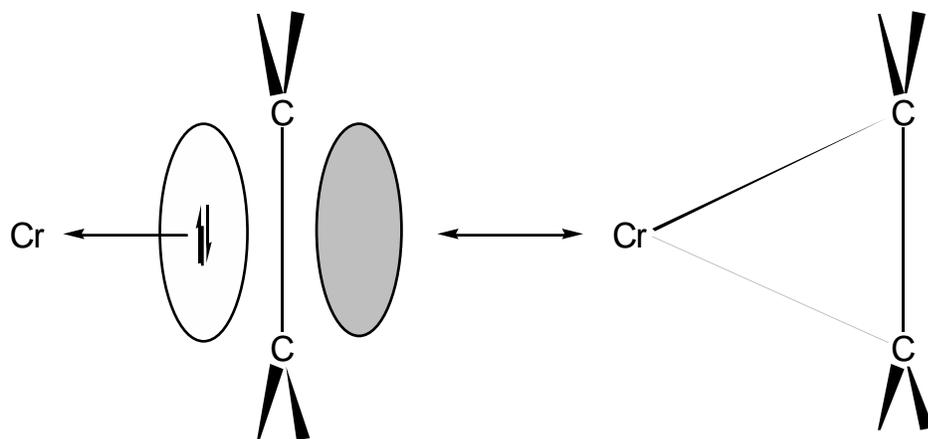


π -Symmetry Interaction: π -Back Donation

In the σ -symmetry component, there is σ -donation from a filled σ -symmetry orbital on the carbonyl (i.e. approximately carbon sp in character) to a vacant σ -symmetry orbital on the chromium (i.e. approximately metal d^{2sp^3} in character). In the two π -symmetry components (one in the xz and one in the yz plane), there is π -back donation from two filled π -symmetry orbitals on the chromium (i.e. approximately metal d_{xz} or d_{yz} in character) to a pair of vacant π -symmetry orbitals on the carbonyl (i.e. approximately the pair of $CO \pi^*$ anti-bonding orbitals in the xz and yz planes, respectively). These so called σ -bonding and π -back bonding interactions are synergic. By this we mean that they mutually reinforce one another (i.e. the whole being greater than the sum of the parts). With electron rich metal centers, σ -donation is mildly reduced, and π -back donation is strongly enhanced. This makes the net Cr-C bond order relatively high (i.e. nearing two) and

the C-O bond order relatively low (i.e. nearing two) corresponding to relatively short Cr-C bonds and long C-O bonds. With electron poor metal centers, σ -donation is mildly enhanced, and π -back donation is strongly reduced. As a result, the net Cr-C bond order is relatively low (i.e. closer to one), and the C-O bond order is relatively high (i.e. closer to three) corresponding to relatively long Cr-C bonds and short C-O bonds. Overall, the direction of net electron transfer is from the chromium center to the carbonyl ligand. Carbonyl ligands are therefore referred to as π -acid ligands.

The bonding between the arene ligands and the chromium center can also be described in terms of complementary valence bond and molecular orbital bonding models. Because of the presence of six bonding atoms and six donor electrons on the arene, these models are significantly more complex than those for carbonyls. However, they are qualitatively similar to those for alkene-metal interactions which are much simpler to understand in detail. For alkenes, the valence bond model describes the bonding in terms of two resonance components, i.e.



Resonance Form I

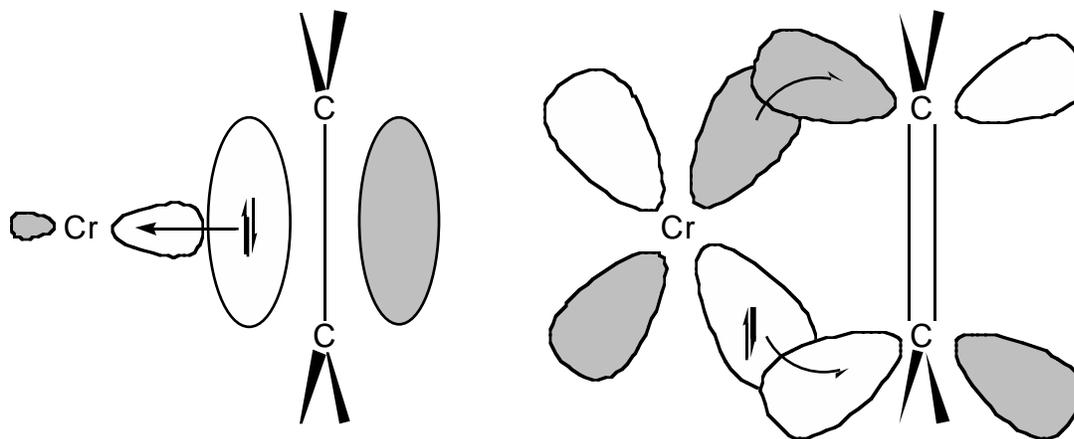
“Alkene Like”

Resonance Form II

“Metallo-Cyclopropane Like”

In the “alkene like” resonance form, the alkene carbons are sp^2 hybridized; while in the “metallo-cyclopropane like” resonance form, the alkene carbons move towards a sp^3 hybridization. Therefore, if the actual electronic structure contains a substantial resonance contribution from the second resonance form, the alkene substituents bend away from the metal due to this rehybridization. For alkenes, increased electron richness on the metal or decreased electron richness on the alkene favor contributions from the second resonance form, while decreased electron richness on the metal or increased electron richness on the alkene favor increased contributions from the first resonance form.

In localized molecular orbital terms (i.e. the Dewar/Chatt/Duncanson model), the bonding is described as a synergistic combination of σ -donation and π -back donation, i.e.



The σ -Symmetry Interaction

σ -Donation

The π -Symmetry Interaction

π -Back Donation

For alkenes, the σ -donation is from a filled σ -symmetry orbital on the alkene (i.e. the alkene π -bonding orbital which is approximately σ -symmetry with respect to the metal) to a vacant σ -symmetry orbital on the chromium (i.e. approximately metal d^2sp^3 in character). In the π -symmetry component, there is π -back donation from a filled π -symmetry orbitals on the chromium (i.e. approximately metal d_{xz} , d_{yz} , or d_{xy} in character) to a vacant π -symmetry orbital on the alkene (i.e. the alkene π^* anti-bonding orbital which is π -symmetry with respect to the metal). Again, increased electron richness on the metal or decreased electron richness on the alkene favor somewhat decreased σ -donation and substantially increased π -back donation, while decreased electron richness on the metal or increased electron richness on the alkene favor somewhat increased σ -donation and substantially decreased π -back donation.

The net effect predicted for either bonding model is that increased contributions from the second resonance form, or increased π -back donation will strengthen the chromium-carbon bond, weaken the alkene carbon-carbon bond, and bend the alkene substituents away from the metal. As with carbonyls, these two interactions are synergic. However, because the alkene is both a better σ -donor and a poor π -acceptor than is a carbonyl, the direction of net electron density transfer is now typically from the alkene to the metal.

Although more complex (2b, c), the basic nature of the chromium-arene bond is analogous to that described above for alkenes with arene to chromium donation and chromium to arene back donation. In particular, arenes are strong net electron donors to the chromium centers, and their bonding has both arene to metal donation and metal to arene back donation, qualitatively similar to that observed for alkenes.

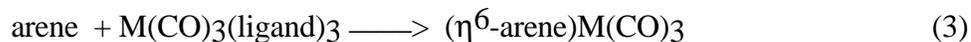
Synthesis of (η^6 -arene)Cr(CO)₃ complexes. A wide variety of different routes have been employed for the synthesis of the congeneric (η^6 -arene)M(CO)₃ (where M = Cr, Mo, and W) complexes (1-4, 6). The greatest range of different routes and different arenes have been used for chromium (i.e. the molybdenum and tungsten complexes being mainly restricted to arenes having no heteroatom substituents).

Some of these syntheses involve the direct reaction of the M(CO)₆ starting materials with the appropriate arene, i.e.



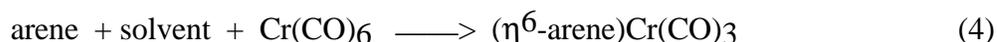
These reactions involve the rate-determining dissociation of a carbonyl ligand from the metal followed by rapid initial arene coordination (i.e. in an η^2 -fashion). The subsequent loss of two additional carbonyl ligands and the concomitant slippage of the arene to first η^4 - and then η^6 -coordination give the observed products. To obtain acceptable overall reaction rates, this rate-determining step must have its rate accelerated. This can be done by several methods, including: heating these reactions to temperatures around or above 100 °C, irradiating the reaction mixtures with ultra violet light, or treating the reaction mixtures with ultrasonic energy. The thermal reactions can be carried out in neat arene solvents for inexpensive liquid aromatics (2d), but, more commonly, they are carried out in a high boiling “inert” solvent. Although high boiling alkanes have been used, ethers such as di-*n*-butyl ether (often containing about 10% THF, see below), diglyme, and dioxane generally appear to be superior for chromium complexes. They give cleaner reactions and shorter reaction times. For this reason pure or mixed ether solvents have been most widely employed.

A related route involves the displacement (generally thermal) of three equivalents of a ligand weaker than the carbonyl group from the M(CO)₃(ligand)₃ complexes, i.e.



Examples of the displaced ligands include nitriles, amines, and other more weakly bound arenes (especially naphthalene).

For chromium, an especially widely used variant of these reactions is to combine the *in situ* generation of the $\text{M}(\text{CO})_3(\text{solvate})_3$ complexes with the arene complexation step, i.e.



The reaction with a solvent mixture of di-*n*-butyl ether and about 10% THF has proven to be particularly useful. The di-*n*-butyl ether provides a high boiling inert solvent from which almost all of the derivatives readily precipitate at room temperature. The THF provides the transient coordinating ligands, increases the reactant and product solubilities, decreases the reaction temperature enough to minimize thermal decomposition, and washes the sublimed $\text{Cr}(\text{CO})_6$ back into the reaction flask.³ Another particularly useful ether solvent is dioxane which fulfills both functions simultaneously. Other commonly used ether solvents such as diglyme and tetraglyme can also be used. Indeed, this hybrid route has been used to prepare over 100 different $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ derivatives (1, 6).

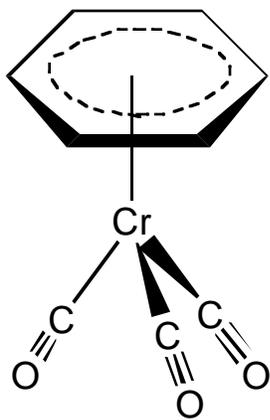
Whichever the route chosen for the synthesis, the reaction progress needs to be monitored to determine when it is completed. This is usually best done by monitoring the reactions by IR where one can observe the carbonyl band due to $\text{M}(\text{CO})_6$ at about 1980 cm^{-1} being replaced by the two or three carbonyl bands characteristic of the target $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes.

³ This, along with the use of *air cooled* condensers, prevents the $\text{Cr}(\text{CO})_6$ (which rapidly sublimates at these temperatures) from building up in the condenser, which it tends to block. This, in turn, prevents several common routes for the reaction to fail.

Structures of (η^6 -arene)Cr(CO)₃ complexes. Arenes can coordinate to one or more metals in a wide variety of fashions (2a). In the η^2 and η^4 (read as the “eta two” and “eta four”) bonding modes there are two and four, respectively, arene carbons within covalent bonding distance of the metal. Thus, they are structurally analogous to coordinated η^2 -cycloalkenes and η^4 -1,3-cyclohexadienes. The η^2 and η^4 bonding modes of arenes are relatively unstable for most complexes due to the partial loss of their aromatic character upon partial coordination to the metal center. Consequently, they are not usually observed in stable complexes. However, they are commonly invoked as reaction intermediates in organometallic arene chemistry. When they are isolated or suspected as intermediates, they display a strong tendency to expel other ligands from the metal’s coordination sphere and so change their coordination mode from η^2 through η^4 to the most stable η^6 (read as “eta six”) form. As would be expected from this argument, by far the most common arene coordination mode in stable complexes is the η^6 bonding mode in which all six of the arene carbons are within covalent bonding distance to the metal. These three bonding modes donate a total of two, four, and six electrons, respectively, to the metal’s eighteen electron count and formally occupy one, two, and three coordination positions about the metal, respectively.

In this experiment, all of the target organometallic (η^6 -arene)Cr(CO)₃ complexes are prepared from simple benzene derivatives. This is because the analogous complexes of condensed-ring aromatics (e.g. (η^6 -naphthalene)Cr(CO)₃ and (η^6 -anthracene)Cr(CO)₃) are generally much less stable and also condensed-ring aromatics tend to be *much* more toxic. On the other hand, these syntheses are very successful with arenes having two or more non-fused benzene rings in the same starting material (e.g. (η^6 -biphenyl)Cr(CO)₃ and (η^6 -diphenylmethane)Cr(CO)₃). With such complexes, however, the reaction purifications are complicated by the fact that mixtures of organometallic products are normally formed. For example, a reaction with 4-amino-4'-methyl-biphenyl would be expected to form three organometallic products: one with a Cr(CO)₃ group on both of the aromatic rings, one with the

Cr(CO)₃ group on the amine substituted ring, and one with the Cr(CO)₃ group on the methyl substituted ring.

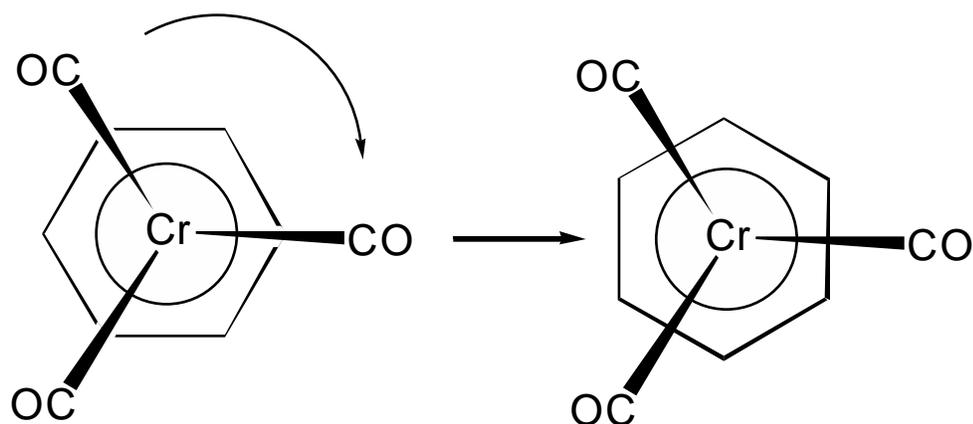


The (η^6 -arene)Cr(CO)₃ complexes were among the first classes of organometallics to receive intensive study during the golden years of explosive growth for transition metal organometallic chemistry (i.e. during the 1950's and early 1960's). It was quickly realized that these complexes had the so called “three-legged piano stool” structures. In these structures, the carbonyl ligands are attached at approximately 90° angles to one another forming the three legs of a tripod while the arene is centered over the metal forming the flat top of the stool (i.e. η^6 bonding). Overall, these complexes have approximately C_{3v} symmetry in the solid state.

These complexes have linear carbonyl groups and nearly planar arenes, three very similar Cr-C(carbonyl) bond distances of about 1.85 Å, three very similar C-O(carbonyl) bond distances of about 1.15 Å, six very similar Cr-C(arene) distances of about 2.25 Å, and six normal aromatic

C-C distances (1b). The observed deviations from equality are normally explained as arising from the effects of the arene substituents on the complexes' electronic structures, the effects of the carbonyls on eclipsed carbons, and crystal packing effects.

In the solid state, the arenes tend to adopt a eclipsed conformation with respect to the carbonyl ligands for arenes having π -donor substituents and staggered conformations for arenes having π -acceptor substituents. In solution, the arene rings rotate rapidly with respect to the carbonyl tripod largely averaging out the effects of the carbonyl ligands on the different parts of the ring, i.e.



Eclipsed Conformation

Staggered Conformation

Bottom View of Complex Showing Arene Rotation with Respect to the Carbonyl Ligands

Similarly, most arene substituents retain the abilities they had in the uncomplexed arenes to rapidly

rotate around the arene-substituent bond. For example, methoxy, amino, and methyl groups still typically freely rotate around their single bonds to the arene rings.

Bonding of (η^6 -arene)Cr(CO)₃ complexes. Elementary treatments of the bonding in these complexes have been presented above. They agree qualitatively with the results of more rigorous molecular orbital calculations. These calculations predict substantial net transfer of electron density from the arene rings through the chromium centers and onto the carbonyl ligands. The greatest net electron transfer is expected to occur for the most electron rich arenes. Indeed, it has been shown that the electron richness of uncomplexed arenes is strongly and linearly correlated with the electron richness of the corresponding (η^6 -arene)Cr(CO)₃ complexes. In addition, these results have consistently shown that the highest occupied molecular orbital, HOMO, of these complexes is metal-carbonyl bonding in character while the lowest unoccupied molecular orbital, LUMO, of these complexes is metal-carbonyl anti-bonding in character.

Physical properties of (η^6 -arene)Cr(CO)₃ complexes. The physical properties of these complexes have been thoroughly documented in the literature. They range in color from pale yellow through orange to almost red with the most electron poor arenes generally giving the most highly orange/red colored materials. Interestingly, solutions of some of these complexes are thermochromic. That is, they reversibly change color as a function of temperature. The most common color change seen is from yellow or pale orange solutions at room temperature to dark orange or even red solutions at elevated temperatures. These compounds are all solids at ambient temperatures and generally have sufficiently high vapor pressures that they can be sublimed under a good vacuum. Under an inert atmosphere, many display reversible melting points in addition to the thermal decomposition observed at higher temperatures. At ambient temperatures, the derivatives of benzene are all thermally stable for an indefinite period when they are sufficiently pure. As noted above, the derivatives of fused ring aromatics are substantially less thermally stable. For examples of transition metal organometallic complexes, which are famous for their air sensitivity, this class of complexes is remarkably air stable. Thus, pure single crystalline samples are normally stable in air for months or years while powdered samples are air stable for hours,

days, or often years.⁴ As one would expect, these materials are much less air stable in solution. Never-the-less, most derivatives are air stable in solution for minutes or hours. Because of this, much of their purification can often be carried out in air, and their IR and NMR spectra can routinely be collected in air if one moves quickly.⁵ [Note: They are quite air sensitive at elevated temperatures, and therefore their syntheses need to be carried out under anaerobic conditions.] The Cr(CO)₃ group in these complexes strongly increases the polarities of complexes derived from non- or weakly-polar arenes (e.g. for alkyl and siloxy aromatics). In general, these complexes are most soluble in polar organic solvents such as dichloromethane, acetone, and tetrahydrofuran and are less soluble in non-polar organic solvents and in strongly hydrogen-bonding solvents such as methanol and water. In this context, it is noteworthy that these complexes don't appear to be particularly water sensitive.⁶ Therefore, rigorous drying of solvents used to prepare, chromatograph, and crystallize these materials is generally not required.

Purification of (η^6 -arene)Cr(CO)₃ complexes. The relatively high stabilities of these complexes means that a wide variety of methods are suitable for their purification. If one has access to a good high vacuum line, these complexes can be purified by fractional sublimation. Any

4 Since powders are almost always less pure than micro-crystalline or crystalline samples (i.e. impurities often catalyze decomposition) and since they have much higher surface areas, powdered samples are almost always more air sensitive than crystalline samples. Indeed, compounds that may be pyrophoric as impure powders may be air stable for years as pure crystalline solids.

5 Their solutions generally give the best results if they are made up immediately prior to use. Those made up one day seldom fail to decompose by the next.

6 This relative water stability is unusual for a transition metal organometallic in a low formal oxidation state. It is a kinetic, rather than a thermodynamic effect, and may be due to the inaccessibility of the metal center to incoming water molecules.

residual $\text{Cr}(\text{CO})_6$ and most liquid arenes are much more volatile than are $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes while solid arenes may be less volatile. The other methods that are generally the most useful are fractional crystallization and column chromatography.

Many of these materials are easily purified by fractional crystallization. One method is to place a solution of these materials that is saturated at room temperature into the freezer. This is often done using a mixed solvent containing some combination of dichloromethane, toluene, and hexanes. A second method is to slowly remove the better and more volatile solvent from a saturated mixed solvent system *in vacuo*. This is often done by evaporating dichloromethane from a saturated solution containing some combination of dichloromethane, toluene, and hexanes. The third method is to place a layer of a less dense and poorer solvent on top of a saturated solution of the complex. This is often done using a layer of toluene or hexanes on top of a saturated dichloromethane solution.

When crystallization isn't successful, column chromatography under an inert atmosphere almost always works. The most widely used column packing materials are silica gel or partially hydrated alumina column packings. The organic eluents are chosen to have an increasing degree of polarity as the chromatography progresses (e.g. by slowly changing the eluent mixture from pure hexanes through toluene, dichloromethane, and tetrahydrofuran in small increments of polarity). Thin layer chromatography, TLC, carried out in air or under dinitrogen in a glove bag is very useful for identifying the best combination of column packings and eluents for a particular system. If one is feeling adventurous, one can also use reverse phase liquid chromatography, gas chromatography, GC, or high performance liquid chromatography, HPLC, to study product mixtures and purify $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes. However, this often results in a ruined column if conditions are not quite right. Therefore, these techniques are only recommended if an old column is available that wouldn't be too badly missed if it "died" in the service of organometallic chemistry.

Compositional characterization, purity determination, and spectroscopic

properties of (η^6 -arene)Cr(CO)₃ complexes. These complexes have relatively simple structures. This, combined with their generally high solubilities and stabilities, means that they are relatively easy to characterize by spectroscopy. In particular, the purity, elemental compositions, and molecular formulae of these complexes can be determined relatively simply.

To confirm that you have obtained the desired target compound and also to provide evidence for gross impurities, C/H/N combustion analysis, perhaps combined with halogen and/or oxygen and/or chromium analysis, is the method of choice. As with other classes of molecules, the American Chemical Society criteria for the establishment of identity and purity requires that calculated and observed analytical numbers agree to within 0.40 %.⁷ With a well behaved pure sample and good analytical techniques, the reproducibility of these analytical values should be at least +/- 0.10%. The observed C/H/N values for many of these complexes, even when they are pure, are occasionally low. In some cases this is due to incomplete combustion. In these case, the addition of a high oxidation state metal oxide combustion additive will usually solve the problem. In other cases this may be due to the presence of solvent molecules in the solid state structures. This is especially common when CH₂Cl₂ has been used in the final crystallization. However, before CH₂Cl₂ molecules of solvation can be legitimately invoked to explain inconsistent analytical data, there must be independent evidence for their existence in the solid sample (e.g. from NMR or x-ray crystallography). Minor impurities and isomeric complexes, on the other hand, are often not detected by elemental analysis. They are best detected, quantified, and identified by spectroscopic methods, particularly mass, IR, and NMR spectroscopy.

The molecular weights of these (η^6 -arene)Cr(CO)₃ complexes can be established by colligative methods. Alternately, they are sufficiently volatile to make their low and high resolution mass spectra easily obtainable (if your departmental mass spectroscopist is willing to have

⁷ Thus, if the calculated carbon content for the pure compound was 46.21%, then an carbon elemental analysis of 46.52% would be acceptable, but one of 46.65% would not.

organometallics placed in their mass spectrometer(s)).⁸ In their mass spectra, the most informative and easiest to interpret features are peaks at the masses of $(P^+ - n28)$. These peaks are due to the parent ion and fragments arising from the successive loss of the carbonyl ligands. The peaks having $n = 1$ and sometimes $n = 0$ (i.e. the parent ion) are often relatively weak while the peak having $n = 3$ (i.e. due to the $(\eta^6\text{-arene})\text{Cr}^+$ fragment) is often the highest (base) peak in the spectrum.

The IR spectra of these $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes have two or three very strong peaks in the metal-carbonyl region. The sharper A_1 symmetry vibration is observed between approximately 2000 and 1950 cm^{-1} while the broad E symmetry vibration is observed at between approximately 1950 and 1850 cm^{-1} (e.g. at 1974 and 1894 cm^{-1} , respectively, for $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in dichloromethane). As expected, these values are lowest for the most electron rich complexes. For less symmetric arene derivatives in solution and for many complexes in the solid state, the E symmetry band is split into two bands. The E symmetry bands are between about two and three times as broad as the A_1 symmetry bands in the same complex and solvent. As expected, all of these bands are sharpest in the least polar solvents and broadest in the solid state. The peak maxima of these bands can also shift by 10 cm^{-1} or more when changing solvents. This is most commonly due to Lewis acid-base interactions between the lone pairs on the carbonyl ligands and Lewis acid sites on the solvents. These carbonyl spectra confirm that the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes have approximate C_{3v} symmetries in both solution and the solid state.

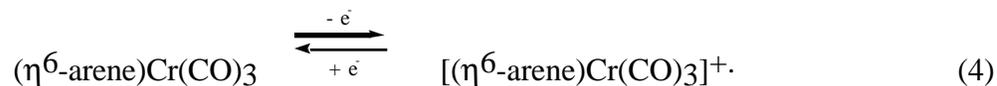
The ^1H and ^{13}C NMR spectra of these $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes confirm that the substitution geometry around the arenes does not change upon coordination, that the center of the arene is approximately symmetrically bound to the metal center, and that the arene ring freely

⁸ Organometallics have a reputation of rapidly degrading mass spectrometer performance resulting in the need for more frequent spectrometer disassembly and cleaning. Consequently, they are often run when spectrometer performance is already partially degraded (i.e. just before regularly scheduled maintenance).

rotates with respect to the carbonyl ligands as do most arene substituents with respect to the aromatic rings. More interestingly, both the proton and carbon resonances due to the arene are shielded with respect to the uncomplexed arenes by about 1 ppm and 35 ppm, respectively. This makes it easy to detect the traces of arene which are commonly seen due to either unreacted starting material or to product decomposition. In addition, the carbonyl carbons are detected at between about 225 and 240 ppm. Surprisingly, the most electron poor complexes give the most shielded carbonyl chemical shifts! [Note: this is due to the perverse effects of the paramagnetic screening terms on the chemical shift tensors in these complexes.]

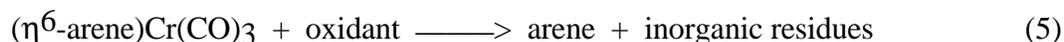
As with any other class of chemicals, the most powerful methods available for determining the structures of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes is X-ray crystallography since it gives detailed bond length and angle and stereochemical information for the whole molecule. Indeed, dozens of these complexes have been so characterized. Due to recent advances in instrumentation, theory, software, and especially, computers, it is becoming increasingly easy to determine a *routine* single crystal structure by X-ray diffraction. Indeed, such determinations can now generally be completed within somewhere between a day and a week after data collection begins. Where one is paying realistic instrument costs, it can actually be both faster and cheaper to get an X-ray structure done than to get and interpret the usual range of “sporting” data (i.e. elemental analysis, MS, IR, and NMR data). The biggest limitation now is often in growing the single crystals in the first place. However, $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes are relatively easy to crystallize (especially those with NH_2 , NR_2 , and CO_2Me groups), and so this is less of a problem here than with many other classes of molecules.

Electrochemical properties of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes. Cyclic voltammetry measures the relative ease and reversibility with which electrons can be added to or removed from a complex in solution. In non-donor solvents (e.g. dichloromethane with tetra-*n*-butylammonium hexafluorophosphate as the support electrolyte), most $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes are reversibly oxidized at potentials of between 0.4 and 1.4 volts with respect to a ferrocene standard (1a), i.e.

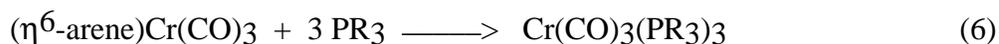


Since the energy of the HOMO of these complexes reflects the electron richness of the complexes, it is not surprising that the most electron rich arenes produce the most electron rich complexes displaying the lowest oxidation potentials. The reversibility of these oxidations are also found to be strongly correlated with arene structure. Thus, the most electron rich arenes having the most steric congestion give $[(\eta^6\text{-arene})\text{Cr}(\text{CO})_3]^+$ radical cations that have the highest thermal stabilities and greatest resistance to decomposition by nucleophiles.

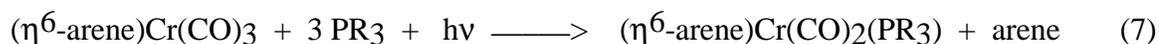
Reactions of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes. The reactions of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes can be divided into several broad categories, including the following: reactions which break the arene-chromium bond, reactions which break chromium-carbonyl bonds, and reactions which change the structure of the coordinated arenes. Heating these complexes or treating them with strong oxidants (e.g. O_2 , I_2 , or Ce^{IV} salts) in solution results in the release of the arene ligand, i.e.



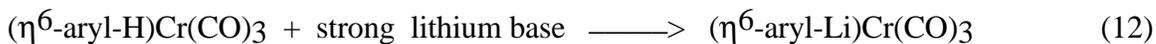
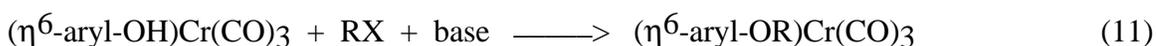
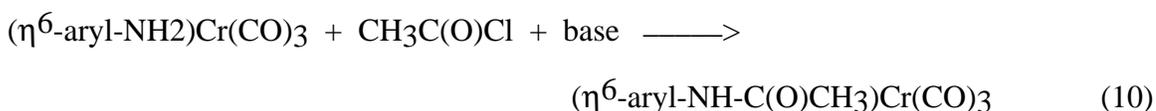
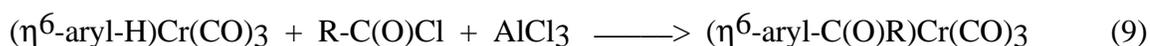
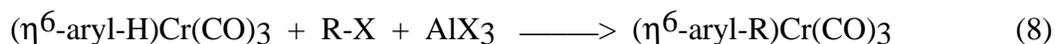
Similarly, the addition of strongly Lewis basic ligands like phosphines or pyridines releases the arene and produces new organometallic complexes as well, i.e.



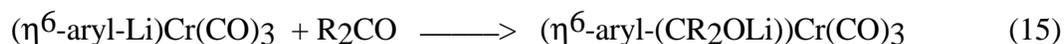
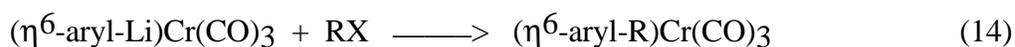
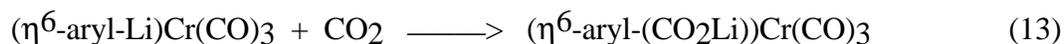
Photolysis of these complexes in the presence of Lewis bases results in the replacement of a carbonyl ligand, i.e.



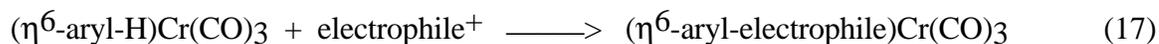
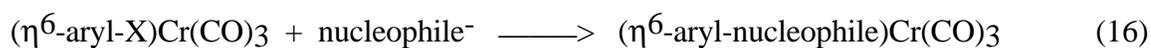
Finally, the coordinated ligands are prone to the common organic reactions observed for their uncomplexed analogues, including the following: Friedel Crafts alkylation and acylation, acylation of amine substituents, and alkylation of phenol hydroxy substituents, and deprotonation by strong bases, i.e.



The latter organochromium organolithium reagents can then react with a wide range of electrophiles, i.e.



These complexes are also prone to reactions involving the replacement of halide substituents by nucleophiles in nucleophilic aromatic substitution, NAS, and hydrogen substituents by electrophiles in electrophilic aromatic substitution, EAS, reactions, i.e.



Since the $\text{Cr}(\text{CO})_3$ group is a net electron withdrawing group similar in ability to a NO_2 group, the $\text{Cr}(\text{CO})_3$ group on the ring enhances NAS and inhibits EAS. These reactions often occur with greater stereo control than is possible on uncomplexed arenes. This is partially due to the fact that complexation of a pro-chiral arene to a $\text{Cr}(\text{CO})_3$ group makes the molecule chiral and partially due to the fact that the $\text{Cr}(\text{CO})_3$ group blocks one face of the arene. Using combinations of these methods, organic chemists can coordinate an arene to the $\text{Cr}(\text{CO})_3$ group, chemically modify its structure in unusual and useful ways, and then cleave it from the chromium center to give a new aromatic compound.

Starting points for student discussion in their laboratory reports. Some question for students to consider as starting points for their discussions include:

(a) Why do the most electron rich complexes give the lowest IR carbonyl stretching frequencies in the IR?

(b) Why do the most electron rich complexes give the most deshielded carbonyl resonances in the ^{13}C NMR?

(c) Explain the reasoning behind your particular choice of purification method and which impurities you think were removed at each stage.

(d) Compare the details of your synthesis and purification with those of other members of your team/class. Try and determine any trends. Based on these trends, suggest what an ideal target molecule would be in terms of its ease of synthesis and purification.

(e) Tabulate your characterization data and compare it to that for related complexes prepared by other members of your team/class.

(f) Comment on any trends you observed in your characterization data in terms of structure/property correlations.

(g) Rationalize why both bulky arenes and electron rich arenes stabilize the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ radical cations. Predict the structure of an especially stable radical cation.

(h) Why are fused ring $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes less stable?

(i) If you prepare the product $(\eta^6\text{-4-NMe}_2\text{-4'-CO}_2\text{Me-biphenyl})\text{Cr}(\text{CO})_3$, which arene ring would the $\text{Cr}(\text{CO})_3$ group preferentially bind to?

Potential Extensions of this Experiment

There are a number of extensions to this experiment that might be considered for adoption by other laboratories. We have tested some of them to a greater or lesser extent as parts of lab classes, as special projects, and as research projects for high-school, undergraduate, and graduate students. They appear to be very promising, certainly enough so to make them excellent topics for “capstone” lab projects in an organic or inorganic synthesis lab or good starting points for future chemical education research projects in our labs or those of others.

If one is interested in having the students carry out multi-step syntheses having a more traditional organic focus, or one is interested in obtaining a larger range of arene starting materials, one can have the students prepare their own aromatic reagents. Electrophilic aromatic substitution (8) or the Williamson ether synthesis (9) using the substituted aromatics or phenols, respectively, found in most organic chemistry stock rooms are good starting points for such labs.

For those interested in multi-step syntheses having a more inorganic focus, (η^6 -arene)Cr(CO)₃ complexes have a well developed derivative chemistry of their own that can also be exploited. Examples of attractive reactions for (η^6 -arene)Cr(CO)₃ complexes include the study of: (a) the non-rigidity of the arenes about the Cr(CO)₃ unit and the arene substituents about the arene, (b) their vacuum pyrolyses to regenerate Cr(CO)₆, (c) their photolysis to give (η^6 -arene)Cr(CO)₂(ligand) derivatives, (d) their thermal reactions with phosphines to give *fac*-Cr(CO)₃(PR₃)₃ complexes, (e) their Lewis acid induced alkylations and acylations to give new (η^6 -arene)Cr(CO)₃ derivatives, (f) their reactions with nucleophiles to give new (η^6 -arene)Cr(CO)₃ derivatives, (g) their in situ deprotonations and subsequent reactions with electrophiles, and (h) the oxidative de-complexation of the arene ligands.

Indeed, one can easily image a lab integrated lab sequence focusing on these compounds that takes up the better part of a quarter or semester and would involve many of the following: the synthesis of a target arene in several steps (perhaps from a natural product like a steroid), its

complexation to $\text{Cr}(\text{CO})_3$, one or more inorganic reactions on this $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex (e.g. reactions (b) to (d), above), organic chemistry on the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex, followed by the de-complexation to give the final arene product. Given the range of reaction, purification, and characterization methods, such a sequence would make an excellent “capstone” chemistry lab experience.

Alternately, a wide range of alkyl aromatics are found in most departmental stock rooms or can be easily prepared (8). Preliminary work in our labs and those of others suggest that these can be successfully reacted with $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ to give a related series of $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ or $(\eta^6\text{-arene})\text{W}(\text{CO})_3$ complexes as discovery research experiments.

Hints on the Reaction Procedures

There have been several reports in *this journal* of general procedures for handling air sensitive materials (10). In addition, several excellent texts provide detailed procedures as well (11). We have tried to develop procedures that as much as possible rely on conventional glassware found in the sophomore organic or senior synthesis labs. Below are a series of tips based on our experience with these reactions.

(a) No cooling water is needed in the reflux condensers for these high boiling solvent systems. Indeed, the use of water cooled condensers tends to cause the $\text{Cr}(\text{CO})_6$ reactants (which always sublime up into the condenser to some degree) to not be efficiently washed back into the reaction flask.⁹

(b) We prefer to use Teflon[®] sleeves or Teflon[®] tape on the ground glass joints of the reaction flask rather than grease. This is because, at the high reflux temperatures employed, some of the grease is inevitably leached into the reaction flask. This contaminates the product and all too commonly produces a “frozen” joint on the flask.

(c) The reaction flask can be heated with either an oil bath or a heating mantle. In either case, make sure the heating source remains just below the level of the solvent to prevent excessive thermal decomposition of the products.¹⁰

(d) The temperature of the oil bath or heating mantle is critical. If it is too low, then the

⁹ The $\text{Cr}(\text{CO})_6$ rapidly sublimates at these temperatures and builds up in the condenser. This tends to block it which, in turn, causes common routes for the reaction to fail.

¹⁰ Note: occasionally the green to black powders which result from thermal decomposition, and presumably contain finely divided metal powders, are pyrophoric. They should therefore always be handled with care. See the Safety Precautions section.

reagents fail to react or the reactions take an unacceptable long period of time to complete. On the other hand, if it is too high, substantial product decomposition occurs giving insoluble green and gray precipitates which are sometimes pyrophoric, which complicate the purification procedure, and which always reduce yields. The best temperatures give a slow boil with the solvent and $\text{Cr}(\text{CO})_6$ condensing about 3 cm up the condenser.

(e) It is important that the flask not be stirred too vigorously. In our hands, the splashing of products onto the flask walls associated with overly vigorous stirring is correlated with poor yields and increased decomposition.

(f) These reaction also seem to proceed best with somewhat oversized flasks (i.e. 2.5 to 3 times the volume of the solvent).

(g) It is important that the reaction flask be kept under a dynamic flow of dinitrogen or argon to sweep the carbon monoxide generated in the reaction out of the flask. However, if the inert gas enters the reaction flask and passes out of the top of the condenser, too much of the more volatile reaction solvent is lost, and the reaction generally fails. The ideal set up has a T-joint connection at the top of the condenser through which dynamic inert gas flow is maintained throughout the synthesis.

(h) Do not dry the reaction solvents with alkali metal benzophenone ketyls (e.g. $\text{Na}/\text{Ph}_2\text{CO}$), as these leave traces of benzene in the solvents that can confound you by giving $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ products. In addition, we find that the di-n-butyl ether and tetrahydrofuran used in these reactions doesn't need to be particularly dry; therefore, fresh samples (i.e. not containing peroxides) can be used without drying with no apparent loss of yield or product purity.

(i) The excess $\text{Cr}(\text{CO})_6$ that sublimates out of the reaction mixture during purification, and/or that which condenses in the solvent trap, can be purified by vacuum sublimation. This gives back $\text{Cr}(\text{CO})_6$ that is "as good as new".

(j) If the final reaction mixture contains visible particulates or has a greenish or grayish cast, filter it through a bed of Celite[®].

(k) Argon can be used as the inert gas but is generally much more costly and provides no noticeable benefit.

Safety Precautions

There are several potential safety hazards associated with these procedures that merit discussion. Like many metal carbonyls, $\text{Cr}(\text{CO})_6$ is a volatile toxic substance. Similarly, many aromatics are carcinogenic and/or are otherwise toxic. Therefore, these materials should only be handled while wearing gloves and in a well ventilated fume hood. The solvent systems used in these reactions boil at or above temperatures of 100 °C. Because of this, only air cooled condensers need be used for the conventional scale syntheses. For the microscale reactions, water cooled condensers may be required. In these cases, ensure that the hoses have been firmly wired in place. This will prevent leaking water from entering the oil bath where it will cause “spitting” which can lead to oil burns. Occasionally when these reactions are overheated, insoluble green/gray residues (presumably finely divided metallic chromium metal) have formed which have ignited paper towels and filter papers after the solvents have evaporated. To prevent this potential fire hazard, thoroughly wet any residues, filter papers, and paper towels used to clean the reaction flask with water before discarding them. Peroxides build up over time in all solvents which are exposed to air particularly when they are very dry. To minimize this hazard, test for peroxides if in doubt, do not use old solvents, do not use overly dry solvents (slightly wet solvents seem to be less prone to peroxide buildup), and store any dry solvents under dinitrogen. As with any syntheses involving air sensitive compounds, pressurized inert gasses are used. If mishandled, pressure buildups can occur resulting in violent breakage of the glassware. Use extreme caution when applying pressure to any system making sure the reaction flasks always have pressure relief available through an *open* bubbler.

General Guidelines for (η^6 -Arene)Cr(CO)₃ Synthesis Reactions

The procedures described below work for essentially any non-fused ring aromatic that is not substantially more electron poor than benzene. In general, the more electron rich the arene the quicker the reaction proceeds. We have found that NH₂ and NR₂ substituents have the strongest accelerating effects followed by OR substituents and then alkyl or aryl substituents. For these groups, the higher the total number of electron donating substituents on the arene, the faster the reaction tends to proceed. Indeed, the use of two or more NH₂/NR₂ groups or one of these and several OR and/or R groups leads to reactions that are almost always done overnight. The use of arenes having several ether an/or alkyl groups gives reactions that typically take one to three days. Any NH₂ and NR₂ substituents also tend to make the products easier to crystallize. Therefore, substituted anilines are the arenes that generally give the quickest and best results. The arenes can also have one or more additional F substituents without the reactions being made substantially slower, but the use of Cl substituents significantly lowers the success rate of these reactions. For chlorinated aromatics, dioxane, rather than Bu₂O/THF, generally appears to be the solvent of choice. Interestingly, we sometimes observe the conversion of chlorine substituents on the arene starting materials to hydrogen atoms on the rings of the products. In our hands, bromo and iodo aromatics are unsuitable for student syntheses since they generally fail under these reaction conditions. The aromatics used can also have one mildly electron-withdrawing substituent (e.g. CO₂R, acyl, or CF₃) in addition to one or more electron donors with acceptable increase in reaction time (giving reactions that take two to four days in general). Indeed, the use of a CO₂Me substituent also tends to increase the crystallinity of the products. However, the use of two or more electron-withdrawing groups tends to cause these reactions to fail under the conditions described below. If the arene has strongly electron-withdrawing groups (e.g. NO₂) or acidic side chains (e.g. CO₂H and SO₃H) on its substituents, the desired products are also not produced in these reactions.

Reagent grade chemicals were purchased from the Aldrich Chemical Company. The dinitrogen and argon gasses were 99.999 % pure. The IR spectra were recorded as CH₂Cl₂ solutions on a Perkin-Elmer 1600 FT IR Spectrometer, and the mass spectra were obtained from a

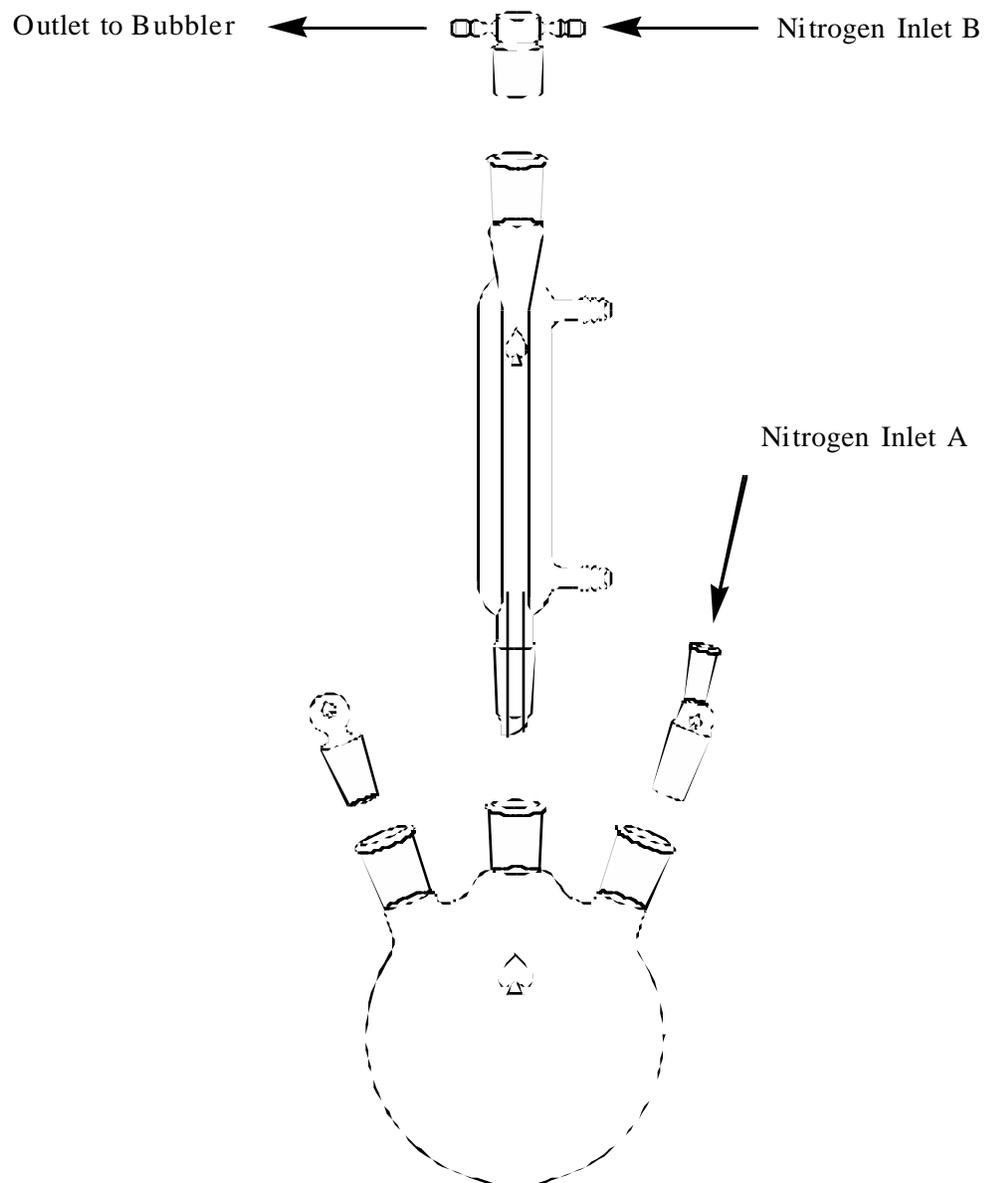
Finnigan 10-20B or GCQ GC/MS Spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Varian Gemini-2000 400 MHz spectrometer and referenced on internal TMS. Related powder and single crystal x-ray diffraction studies were carried out on Siemens P4 diffractometers, one equipped with a X-1000 multi-wire area detector.

Typical Equipment List for Conventional Scale Syntheses

We typically use 24/40 or 19/38 glassware but 14/20 or 14/10 glassware works equally well. The following is a list of items each student will need:

- (1) one three necked round bottom flask (we have used 100 to 1,000 mL flasks)
- (2) one Teflon[®] coated stir bar
- (3) one gas inlet adapter equipped with a stop cock or a hose clamp
- (4) two glass stoppers
- (5) one rubber septum
- (6) one reflux condenser
- (7) one T-shaped adapter
- (8) one mineral oil bubbler
- (9) two syringe needles (one about 3 cm and one about 10 or more cm in length)
- (10) a Buchner funnel and filter paper or a fritted glass funnel
- (11) (optional) a Schlenk tube for crystallization and drying of compounds

Expanded View of a Typical Reaction Assembly for Conventional Scale Syntheses



Conventional Scale Preparations of (η^6 -Arene)Cr(CO)₃ Complexes

All of these reactions using relatively electron rich arenes are carried out similarly. A general description of the reaction and purification procedure and apparatus is followed by representative examples chosen to illustrate variations to the general approaches used in specific syntheses.

Generic Procedure for the synthesis of (η^6 -arene)Cr(CO)₃ complexes on a Multi-gram scale. Although these syntheses can be carried out many ways depending on the available glassware and individual preferences, they all follow the same basic procedure outlined below:

(1a) If you will be using solvents that have previously had their O₂ removed use step (1a) first, if not use (1b) first. Set up the required glassware (see above figure) under an inert atmosphere.

(1b) Set up the required glassware in air. Add the required solvents and then bubble inert gas through them to remove dissolved O₂.

(2) Introduce the desired arene and Cr(CO)₆ through on side arm of the reaction flask.

(3) Turn on the stir plate and heating mantle, making sure that no splashing or over heating occurs.

(4) Continue heating the reaction to completion (from 12 to 72 hours, 20 hours being typical).

(5) Monitor the reaction to determine when it has gone to completion. This can be partially done visually by watching color changes and changes in the amount of white solid Cr(CO)₆ sublimed into the reflux condenser. It is best done by monitoring the reaction by IR

where one can observe the carbonyl band due to $\text{Cr}(\text{CO})_6$ at about 1980 cm^{-1} being replaced by the two or three carbonyl bands characteristic of the target $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes.

(6) Remove the heating mantle or oil bath and allow the reaction to cool to ambient temperature.

(7) If substantial quantities of solid product precipitate from the cooled solution, remove the reflux condenser and reduce the volume of the solvent in the flask in vacuo (i.e. to remove the THF). Collect the resulting solid product by filtration in air and recrystallize it from CH_2Cl_2 /hexanes if required.

(8) If no significant product precipitates from the reaction mixture or if it is contaminated by insoluble gray or green solids, remove the reflux condenser and filter the solution in air to remove insoluble particulates (filter the solution through a bed of Celite[®] if the reaction mixture is especially dirty). Use some CH_2Cl_2 wash to dissolve any product from the precipitate and carry it through the filter if necessary. Concentrate the combined filtrates to dryness in vacuo and crystallize the resulting product from CH_2Cl_2 /hexanes.

Synthesis of $(\eta^6\text{-para-phenylenediamine})\text{Cr}(\text{CO})_3$. A gas inlet (inlet A in the diagram) was connected to a dinitrogen source via a latex hose and flushed with this inert gas, and then the stopcock was closed leaving the line under a positive dinitrogen pressure. This gas inlet was placed in one side arm of a 500 mL three-necked round bottom flask. The other side arm of this flask was fitted with a glass stopper while a rubber septum was placed loosely in the center joint. Through this center joint was added di-n-butyl ether (101 mL) and THF (10.5 mL). The rubber septum was then placed back in the joint. A short stainless steel needle was placed through the septum and connected to a mineral oil bubbler via a latex hose. A long stainless steel needle through which was passing a steady flow of nitrogen was then placed through the septum so that it touched the flask bottom. [**Caution:** *never* apply pressure to a closed system, always check that there is an outlet *open* to the bubbler.] The flask was purged with dinitrogen for ten minutes.

[Note: the proper dinitrogen flow rate results in a solution that looks like it is at a very vigorous rolling boil.] Then, the dinitrogen flow through the needle was reduced to about 60 mL/min; the stopcock on the gas inlet was opened; the nitrogen supply needle was removed and finally the exhaust needle was removed. After turning up the dinitrogen flow rate through the side arm to about 200 mL/min, the rubber septum was removed and replaced by a strait reflux condenser topped by a T-adaptor joint. This apparatus was purged with dinitrogen for about one minute. Then, a nitrogen inlet hose was attached to one side of the T- joint (inlet B in the diagram), and a bubbler was attached to the other side. The reaction flask was then charged with a Teflon[®] coated stir bar, chromium hexacarbonyl (3.36 g, 15.3 mmol), and *para*-phenylenediamine (1.50 g, 13.9 mmol) through the side arm. The stopcock on the gas inlet was then closed so that the only nitrogen supply to the reaction vessel was through the T- joint on top. The dinitrogen flow rate was then reduced to about 10 mL/min, and a heating mantle was placed around the reaction flask. Care was taken to ensure that the heating mantle was just below the level of the unstirred solvent. The flask was *gently* stirred using a stir plate and the variable transformer connected to the heating mantle at a setting which maintained a gentle reflux (i.e. about 45% to 60% on the variable transformer). As the reaction mixture neared reflux, most of the Cr(CO)₆ sublimed out of the flask and condensed about 3 cm up the condenser, where the refluxing solvent continually washed it back into the reaction flask. The solution rapidly became lemon yellow in color, and after 41 hours the dinitrogen flow rate was increased to about 60 mL/min, and the heating was stopped. As the reaction cooled, the yellow product precipitated along with some white crystals of Cr(CO)₆. The stopcock on the side arm was opened, and then the condenser was removed under a positive flow of dinitrogen and replaced by a glass stopper. The gas inlet was then connected to a vacuum pump, and the stirred vessel was placed under vacuum for about 20 min at which point all of the residual Cr(CO)₆ and the remaining THF solvent had condensed in the vacuum trap for recycling and disposal, respectively. This left behind a yellow crystalline solid suspended in a pale yellow solution. The yellow crystals of the desired product, (η^6 -1,4-C₆H₄(NH₂)₂)Cr(CO)₃, were collected by suction filtration in air, washed with hexanes (50 mL), and allowed to air dry for one hour. The weight of the crystals was 4.81 g (19.7 mmol, 97% of the theoretical yield). This product is generally analytically pure and can be used for characterization studies and subsequent reactions. However, some batches of this product are contaminated by small amounts of dark

green/gray insoluble solids. These are best removed by filtration through a bed of Celite[®] and recrystallization of the product from CH₂Cl₂/hexanes.

We chose this 41 hour reaction time to fit with our students schedules where they set up the reactions one afternoon and work them up the morning of the second day (i.e. we have two lab periods a week which are two days apart). A somewhat shorter reaction time did not appear to adversely effect the yield. Indeed, the use of a larger excess of Cr(CO)₆ (e.g. 50 to 100%) or of arene (for inexpensive liquid arenes) allowed these reactions to go to completion after 20 hours (i.e. this is best if lab times are on sequential days).

Synthesis of (η^6 -N,N-dimethylaniline)Cr(CO)₃. The reaction apparatus (see diagram above) having a 200 mL reaction flask was assembled under dinitrogen. To this flask were added Cr(CO)₆ (10.0 g, 45.5 mmol), N,N-dimethylaniline (10.0 mL, 9.56 g, 78.9 mmol), Bu₂O (80 mL), and THF (10 mL). The stirrer and heating mantle were then turned on, and the reaction was refluxed for 20 hours at which point all of the Cr(CO)₆ was consumed. After heating was stopped, the yellow crystalline solid precipitated from the lemon yellow solution. The contents of the flask were stirred under vacuum for one hour. Then, the product was collected by filtration in air, washed with petroleum ether (100 mL), and dried *in vacuo* to give (η^6 -C₆H₅(NMe₂))Cr(CO)₃ as fine yellow needles (11.1 g, 43.1 mmol, 94.7%).

Synthesis of (η^6 -N,N-diethylaniline)Cr(CO)₃. The reaction apparatus (see diagram above) having a 300 mL reaction flask was assembled under dinitrogen. To this flask were added Cr(CO)₆ (4.24 g, 19.3 mmol), N,N-diethylaniline (2.8 mL, 17.5 mmol), Bu₂O (100 mL), and THF (15 mL). The stirrer and heating mantle were then turned on, and the reaction was refluxed for 20 hours at which point all of the Cr(CO)₆ was consumed, and the solution was orange in color. After heating was stopped, the solution became yellow. The contents of the flask were filtered in air to remove any particulates. The resulting solution was taken to dryness on a rotary evaporator. Recrystallization of the resulting solid from a minimum of CH₂Cl₂/hexanes

gave a yellow crystalline product that was collected by filtration in air, washed with hexanes (100 mL), and dried *in vacuo* to give $(\eta^6\text{-C}_6\text{H}_5(\text{NEt}_2))\text{Cr}(\text{CO})_3$ in good yield (3.50 g, 70%).

Synthesis of $(\eta^6\text{-methyl-3,5-dimethoxybenzoate})\text{Cr}(\text{CO})_3$. The reaction apparatus (see diagram above) having a 250 mL reaction flask were assembled under dinitrogen. To this flask were added $\text{Cr}(\text{CO})_6$ (2.87 g, 13.0 mmol), methyl-3,5-dimethoxybenzoate (1.72 g, 8.77 mmol), Bu_2O (80 mL), and THF (10 mL). The stirrer and heating mantle were then turned on, and the reaction was refluxed for 70 hours at which point the solution was deep red in color. Upon cooling, the solution was an orange/brown color. The contents of the flask were suction filtered in air, and the brown solid was washed with CH_2Cl_2 (about 50 mL). The resulting combined maroon filtrate was taken to dryness on a rotary evaporator. Recrystallization of the resulting yellow/orange powder from a minimum of CH_2Cl_2 /hexanes gave a yellow/orange crystalline product that was collected by filtration in air, washed with hexanes (50 mL), and dried *in vacuo* to give $(\eta^6\text{-3,5-C}_6\text{H}_3((\text{OMe})_2(\text{CO}_2\text{Me}))\text{Cr}(\text{CO})_3$ in good yield (2.5 g, 86%).

Typical Equipment List for Microscale Syntheses of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ Complexes

We used 14/10 glassware from Ace Glass for these reactions, but any of the commercial or home made microscale glassware kits should work.

- (1) one pear shaped or round bottom flask of 5 or 10 mL volume.
- (2) one Teflon[®] coated stir vane or stir bar
- (3) two rubber septum
- (4) one reflux condenser
- (5) one Y-shaped adapter
- (6) one mineral oil bubbler
- (7) two syringe needles (about 5 cm in length)
- (8) a Buchner funnel and filter paper or a fritted glass funnel
- (9) (optional) a Schlenk tube for crystallization and drying of compounds

Microscale Preparation of the (η^6 -Arene)Cr(CO)₃ Complexes

Although we have done much less work with microscale glassware, it appears to hold particular promise in terms of (a) generally shorter reaction times for equivalent reactions, (b) simpler reaction assembly requiring less fume hood space, (c) a smaller list of required equipment and (d) smaller quantities of reagents required. The major drawback we have seen is a direct consequence of the small scale. We found it somewhat more difficult to work with air sensitive materials (especially in terms of characterization) at microscales. However, this probably reflects our limited experience with microscale procedures more than inherent drawbacks. All of the micro scale syntheses of relatively electron rich (η^6 -arene)Cr(CO)₃ complexes were carried out similarly. A representative example is reported to illustrate the general approach used in these syntheses. It is noteworthy that we had great difficulty preparing this compound in conventional scale reactions. Indeed, based on our limited experience we expect that further work will show that these smaller scale organometallic reactions will generally proceed faster and with less product decomposition.

Synthesis of (η^6 -4-tert-butyl-2,6-dimethylphenol)Cr(CO)₃. A one-neck 10 mL round bottom flask was equipped with a magnetic spin vane and a condenser to the top of which was added Y-adapter having rubber septa on each arm (see diagram below). A dinitrogen supply line was connected to the reaction flask via a latex rubber hose, and a needle inserted into one septum. A dinitrogen exit line connected to a mineral oil bubbler via a latex rubber hose was connected to the reaction flask via a second needle into the other septum on the Y-adapter. This was charged with η^6 -4-tert-butyl-2,6-dimethylphenol (0.20 g, 1.10 mmol) and Cr(CO)₆ (0.35 g, 1.60 mmol). The apparatus was flushed with dinitrogen for 15 minutes, and then de-oxygenated dioxane (6 mL) was added through the septum. The mixture was stirred at reflux (a silicone oil bath was used for heating) for 72 hours to yield a yellow solution. The solution was evaporated to dryness by passing a strong stream of dinitrogen over it just above the heated solution. The resulting yellow solid was identified as (η^6 -4-tert-butyl-2,6-dimethylphenol)Cr(CO)₃ and was obtained in quantitative yield.

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Tables of Representative Data for (η^6 -Arene)Cr(CO)₃ Complexes

Characterization data collected under similar conditions for over five dozen (η^6 -arene)Cr(CO)₃ complexes are tabulated. These data are also very useful for illustrating concepts of structure, bonding, and organometallic spectroscopy in lectures and for constructing problem set examples and exam questions. This *data* was originally submitted along with reference 1a where Table 1 appeared in print and Table 2 was made available as supplementary material. This data is reproduced here to aid instructors and students wanting to use the data.