η^6 -(arene)tricarbonylchromium complex[1]

The η^6 -(arene)tricarbonylchromium complexes were prepared according to a known procedure,[2] by refluxing 5 mmol of the arene and 6 mmol of $Cr(CO)_6$ in a mixture of dibutyl ether (20 mL) and THF (2 mL) for 24-36 h. ^{1}H NMR analyses showed that the conversion never exceeded 30% and that partial dechlorination of the chromium complex had occurred (the extent of which increased significantly on prolonged heating). Increasing the amount of $Cr(CO)_6$ did not lead to improved product yields. After evaporation of the solvents in vacuo, the residue was suspended in ether and filtered. In the case of chlorobenzene and 1,3-dichlorobenzene the filtrate was concentrated to ca. 10 mL volume and hexane (20 mL) was added. Subsequent slow evaporation of the solvents caused precipitation of yellow crystals, which were filtered off and dried. In the case of functionalized chloroarenes, the filtrate was evaporated, coevaporated with toluene, and subjected to column chromatography. This allowed separation of the target complexes from both unreacted arene and the corresponding dechlorinated complex (the latter had a lower R_f -value than the chloroarene complex).

η^6 -(arene)tricarbonylchromium complex[2]

Most simple arenes react smoothly with $Cr(CO)_6$ to give hexahapto complexes.
Caution. The reaction should be carried out in a well ventilated hood, as hexacarbonylchromium is toxic and carbon monoxide is evolved during the reaction. Both ether solvents peroxidize; they should be carefully freed from peroxide and dried (convenielilly by distilling from lithium tetrahydridoaluminate or from sodium) before use. Benzene is toxic; contact with the liquid or vapor should be avoided.

In a 250-mL, round-bottomed flask fitted with a gas inlet and a simple reflux condenser [not spiral or similar type from which subliming Cr(CO)6 is washed back less efficiently] are placed hexacarbonylchrorniurn (4 g, 18 mmole), anisole (25 mL), dibutyl ether (120 mL) and tetrahydrofuran (10 mL). A bubbler is placed at the top of the condenser to prevent access of air. The apparatus is thorougtly purged with nitrogen. The nitrogen stream is stopped and the mixture is then heated at reflux for 24 hours (the checkers found stirring beneficial). The yellow solution is cooled and filtered through kieselguhr (diatomeaceous earth) or a similar material (the checkers used Celite or, preferably, a small pad of anhydrous silica gel) on a sintered-glass filter, which is then washed with a little additional solvent. The solvents are distilled off on a rotary evaporator frorn a water bath held at 60°C (an oil pump may be required to remove the solvents completely); a deep-yellow oil remains to which dry light petroleum ether (bp. 40-60°C or hexane (20 mL) is added. Crystalline (η^6- anisole)tricarbonylchromium [4.1 g (92%), mp 83-84°C] separates. A small amount of unreacted $Cr(CO)_6$ may be recoverable from the condenser; the remainder distills off with thc solvent. If a very pure product is required the compound may be recrystallized by dissolving it in benzene or in diethyl ether and adding light petroleum ether to give 3.53 g (80 %), mp 84-85°C; lit.[6] mp 84-85°C. Anal. Calcd. for $C_{10}H_8CrO_4$: C, 49.2; H, 3.3. Found: C, 49.5 ; H, 3.4.

Solutions of this compound and other arenetricarbonylchronliunis can only be handled for very brief periods in air. The workup procedures are therefore best carried out in an inert atmosphere throughout, but they can be conducted in air if done rapidly and efficiently.

Other Arenetricarbonylchromium Complexes

Table 1 Reaction of arenes with 4 g of $Cr(CO)_6$ to give the corresponding (η^6 -arene)$Cr(CO)_3$ complexes using the procedure given for [η^6-MeOC6H4]$Cr(CO)_3$ except for the conditions noted

Arene	Vol	Reflux time	$Cr(CO)_6$ recovered	Yield		mp	ν_{CO} peaks

	mL	h	g	g	%	°C	cm^{-1}
C_6H_5Cl	20	20	0.35	2.6	64[1]	101-102	1991, 1929, 1925

1 Organometallics 1999 1318
2 Mahaffy, C. A. L.; Pauson, P. L. Inorg. Synth. 1979, 19, 154.

[1] Slight decomposition during the reaction indicated by formation of grey-green precipitateswas found difficult to avoid with chlorobenzene and some arenes. This appears to become progressive and reaction should be stopped and solution filtered when such precipitate is observed.