SYNTHESIS OF TRICARBONYL(DIACETYLARENE)CHROMIUM AND TRICARBONYL(DIFORMYLARENE)CHROMIUM COMPLEXES

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Tricarbonylchromium complexes of diacetylbenzenes and 2,2′-diacetylbiphenyl were prepared in reasonable yields by direct complexation of the starting materials. Tricarbonylchromium complexes of diformylbenzenes and 2,2′-diformylbiphenyl were prepared in good yields by the complexation of the corresponding dioxolanes followed by acidic hydrolysis of the protective groups.

Keywords: Tricarbonylchromium complexes; Arene complexes; Aldehydes; Ketones; Diacetylarenes; Diformylarenes; Biaryls; Chromium hexacarbonyl.

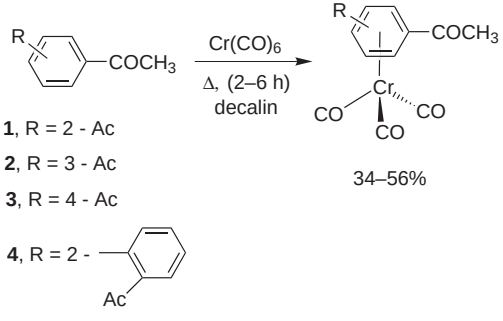
A number of arenetricarbonylchromium complexes has been described in the literature[1,2], but most of them are just monosubstituted benzenetricarbonylchromium derivatives, which were prepared by the Pauson–Mahaffy[3] or Top–Jaouen[4] method. Several years ago, we published a modified method for the complexation of arenes and their derivatives[5–8], which works well for the complexation of some aromatic ketones and esters. The method consists in heating the mixture of an arene, hexacarbonylchromium and a catalyst (butyl acetate or ethyl formate) in decalin to reflux in a special adapter, which precludes the contact of the hot reaction mixture with the atmosphere.

The main goal of this work was to examine whether the method is also suitable for the synthesis of tricarbonylchromium complexes of diacetylarenes and diformylarenes. From this class of compounds, only an inefficient (10% yield) synthesis of tricarbonyl(1,2-diacetylbenzene)chromium was described[9] *via* methylmagnesium iodide addition to tricarbonyl[η^6-(dimethyl phthalate)]chromium. Similarly, tricarbonyl(η^6-terephthalaldehyde)chromium[9,10] was prepared in a low yield *via* the complexation of terephthalaldehyde tetraethyl acetal and subsequent hydrolysis. The synthesis of tricarbonyl(η^6-phthalaldehyde)chromium complex was described as a result of a complex one-pot reaction starting from (η^6-benzene)tri-

carbonylchromium[11]. The tricarbonylchromium complex of 2,2′-(diformyl)-6-methoxybiphenyl has been prepared recently by the Suzuki coupling of (η^6-2-bromo-6-methoxybenzaldehyde)tricarbonylchromium with 2-formylbenzeneboronic acid[12].

RESULTS AND DISCUSSION

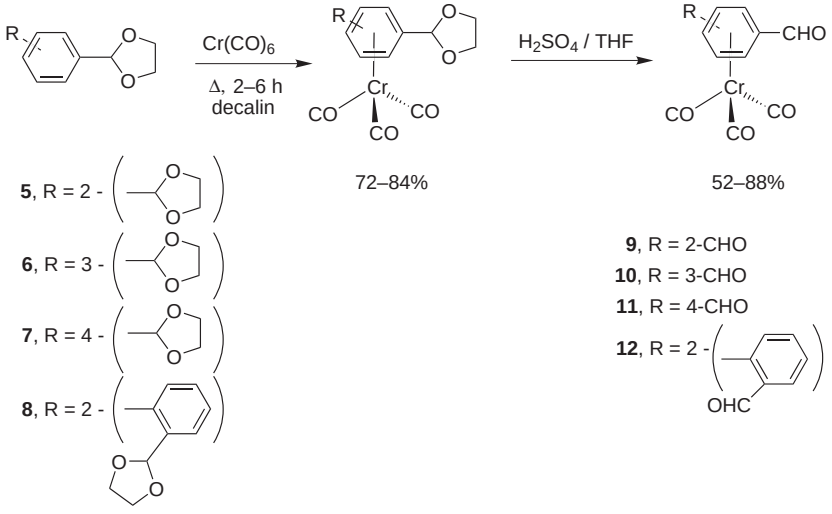
We decided to examine the direct complexation of diacetylarenes with $Cr(CO)_6$ first. The complexations went smoothly; the results are depicted in Scheme 1. The yields of the products strongly depended on the purity of the solvent (decahydronaphthalene), and the reagents (diacetylarenes and hexacarbonylchromium). For example, we obtained 34–56% yields of crystalline tricarbonyl(η^6-1,3-diacetylbenzene)chromium. It is interesting to note that the method could also be applied to a rapid synthesis of tricarbonyl(η^6-indan-1-one)chromium (79% in 5 h) and tricarbonyl(η^6-1,2,3,4-tetrahydronaphthalen-1-one)chromium (51% in 5 h), while tricarbonyl(η^6-1,2,3,4-tetrahydronaphthalen-2-one)chromium was prepared by the complexation of the corresponding dioxolane[13]. Direct complexation is not suitable for the synthesis of tricarbonyl(η^6-indane-1,3-dione)-chromium, either; this compound can only be prepared by the complexation of the bisdioxolane derived from indane-1,3-dione[14,15].



SCHEME 1
Synthesis of tricarbonyl(diacetylarene)chromium complexes

It is well known that the direct complexation of arenes having an aldehyde functional group is not possible and therefore we prepared the bisdioxolanes of the corresponding dialdehydes first. The protection of the aldehyde groups went smoothly and gave high yields (72–84%) of the

bisdioxolanes. The complexation of the bisdioxolanes led to 52–88% isolated yields of the complexes (Scheme 2).



SCHEME 2
Synthesis of tricarbonyl(diformylarene)chromium complexes

The hydrolysis of the tricarbonylchromium complexes of the bisdioxolanes was often accompanied by their decomposition. Thus, we checked several deprotection procedures using concentrated HCl/acetone[16], 85% H_3PO_4/ethanol[17], 85% H_3PO_4/neutral alumina and microwave irradiation (MWI)[18], 4-methylbenzene-1-sulfonic acid (PTSA)/acetone[19], but the best results were achieved using 50% H_2SO_4/THF [15].

In summary, we have succeeded in the preparation of tricarbonylchromium complexes of selected diacylarenes by direct complexation, and developed a method for the synthesis of the complexes of arenes possessing an aldehyde moiety.

EXPERIMENTAL

Chemicals and solvents were purified by standard techniques. ^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ at room temperature on a Varian Gemini 2000 spectrometer at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts are given in δ relative to TMS (δ 0 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77 ppm) for ^{13}C NMR. Coupling constants (*J*) are given in Hz. IR spectra (wavenumbers in cm^{-1}) were measured on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. All melting points are uncorrected, and were measured on a Koffler hot-plate apparatus. All complexations were carried out in a reactor described previously[5–8].

General Procedure for the Complexation of Diacetylarenes (**1**–**4**)

A solution of the corresponding diacetylarene (3 mmol) and $Cr(CO)_6$ (0.66 g, 3 mmol) in decahydronaphthalene (≈70 ml) under Ar was heated at reflux at bath temperature of 265 °C (Wood metal bath) with a catalytic amount of ethyl formate (1 ml). Following the evolution of a calculated amount of CO (≈200 cm^3), the reaction mixture was cooled to room temperature, filtered through a pad of silica gel, washed with hexane (removing decahydronaphthalene) and the product was eluted with Et_2O. The solvent was evaporated and the residue purified by flash-chromatography (SiO_2, hexane–ethyl acetate 3:1) and recrystallized from hexane–Et_2O mixture.

Tricarbonyl(η^6-1,2-diacetylbenzene)chromium (**1**): 232 mg (26%) of orange crystals was isolated, m.p. 63 °C (in accord with ref.[9]). IR: 1972, 1896, 1678, 1252. ^{1}H NMR: 2.48 s, 6 H ($COCH_3$); 5.42–5.47 m, 2 H (Hβ); 5.50–5.55 m, 2 H (Hα). ^{13}C NMR: 28.6, 90.8, 91.0, 105.0, 197.7, 229.7. For $C_{13}H_{10}CrO_5$ (298.2) calculated: 52.36% C, 3.38% H; found: 52.30% C, 3.32% H.

Tricarbonyl(η^6-1,3-diacetylbenzene)chromium (**2**): 304 mg (34%) of orange crystals was isolated, m.p. 118–120 °C. IR: 1975, 1903, 1681, 1220. ^{1}H NMR: 2.51 s, 6 H ($COCH_3$); 5.32 t, 1 H, $^3J_{4,5} = {}^3J_{5,6}$ = 6.6 (H5); 6.32 dd, 2 H (H4,6); 6.72 d, 1 H, $^4J_{2,4} = {}^4J_{2,6}$ = 1.3 (H2). ^{13}C NMR: 25.7, 87.6, 94.4, 94.4, 95.4, 194.2, 228.0. For $C_{13}H_{10}CrO_5$ (298.2) calculated: 52.36% C, 3.38% H; found: 52.27% C, 3.25% H.

Tricarbonyl(η^6-1,4-diacetylbenzene)chromium (**3**): 179 mg (20%) of red crystals was obtained, m.p. 125–127 °C. IR: 1974, 1901, 1683, 1260. ^{1}H NMR: 2.51 s, 6 H ($COCH_3$); 6.00 s, 4 H (H-Ar). ^{13}C NMR: 25.8, 91.4, 97.9, 195.5, 229.4. For $C_{13}H_{10}CrO_5$ (298.2) calculated: 52.36% C, 3.38% H; found: 52.28% C, 3.22% H.

Tricarbonyl(η^6-2,2′-diacetylbiphenyl)chromium (**4**): 258 mg (23%) of orange crystals was isolated, m.p. 113–115 °C. IR: 1963, 1883, 1685, 1246. ^{1}H NMR: 2.18 s, 3 H ($COCH_3$*); 2.49 s, 3 H ($COCH_3$); 5.27 dd, 1 H, $^3J_{5,6}$ = 6.0, $^4J_{4,6}$ = 1.4 (H6*); 5.50–5.60 m, 2 H (H4,5*); 5.75 dd, 1 H, $^3J_{3,4}$ = 6.1, $^4J_{3,5}$ = 1.4 (H3*); 7.49–7.79 m, 4 H (H-Ar) (* corresponding to the chemical shifts of the complexed benzene moiety). ^{13}C NMR: 28.2, 28.7, 91.1, 91.2, 92.5, 96.5, 102.2, 116.2, 127.8, 128.9, 130.9, 131.2, 138.8, 140.8, 197.4, 200.0, 231.5. For $C_{19}H_{14}CrO_5$ (374.3) calculated: 60.97% C, 3.77% H; found: 60.91% C, 3.80% H.

General Procedure for the Preparation of Dioxolanes from the Coresponding Aldehydes

A solution of a dialdehyde (10 mmol), ethylene glycol (1.3 ml, 22 mmol, 1.1 equivalent) and a catalytic amount of 4-methylbenzene-1-sulfonic acid (5 mg) in benzene (20 ml) was heated at reflux under a condenser equipped with the Dean–Stark trap for 15 h. The reaction mixture was cooled to room temperature, washed with 5% NaOH solution and the water layer extracted with benzene (20 ml). The combined organic layers were dried over anhydrous K_2CO_3, and the solvent evaporated. The residue was purified as described below.

1,2-Di(1,3-dioxolan-2-yl)benzene: bulb-to-bulb distillation afforded 1.86 g (84%) of a colorless liquid, b.p. 160 °C/130 Pa. IR: 667, 731, 1073, 1191, 1285, 1373, 1445, 2885. ^{1}H NMR: 4.02–4.17 m, 8 H (OCH_2CH_2O); 6.24 s, 2 H (CH); 7.39 m, 2 H (Hβ); 7.64 m, 2 H (Hα).^{13}C NMR: 63.45, 102.92, 129.20, 127.69, 138.30. For $C_{12}H_{14}O_4$ (222.2) calculated: 64.85% C, 6.35% H; found: 64.82% C, 6.33% H.

1,3-Di(1,3-dioxolan-2-yl)benzene: bulb-to-bulb distillation afforded 1.82 g (82%) of a colorless liquid, b.p. 180°C/130 Pa. IR: 678, 732, 1074, 1194, 1244, 1372, 1447, 2881. ^{1}H NMR: 3.99–4.13 m, 8 H (OCH_2CH_2O); 5.83 s, 2 H (CH); 7.37 m, 1 H (H5); 7.46–7.49 m, 2 H

(H4,6); 7.59 bs, 1 H (H2). ^{13}C NMR: 65.11, 103.31, 124.44, 127.07, 128.25, 138.39. For $C_{12}H_{14}O_4$ (222.2) calculated: 64.85% C, 6.35% H; found: 64.90% C, 6.37% H.

1,4-Di(1,3-dioxolan-2-yl)benzene: recrystallization from a hexane–ethyl acetate mixture gave 1.80 g (81%) of a pale yellow crystalline compound, m.p. 89–90 °C (ref.[20] gives m.p. 89–90 °C). ^{1}H NMR: 4.02–4.11 m, 8 H (OCH_2CH_2O); 5.84 s, 2 H (CH); 7.50 s, 4 H (H-Ar).

2,2′-Di(1,3-dioxolan-2-yl)bifenyl: flash chromatography (SiO_2, hexane–ethyl acetate 5:1) and subsequent recrystallization from hexane furnished 2.15 g (72%) of a colorless crystalline compound, m.p. 52 °C (ref.[21] gives m.p. 52 °C). ^{1}H NMR: 3.80–4.06 m, 8 H (OCH_2CH_2O); 5.50 s, 2 H (CH); 7.24 m, 2 H (H6); 7.38–7.43 m, 4 H (H4,5); 7.67 m, 2 H (H3).

General Procedure for the Complexation of Di(1,3-dioxolan-2-yl)arenes **5**–**8**

A solution of the corresponding bisdioxolane (3 mmol) and $Cr(CO)_6$ (0.66 g, 3 mmol) in decahydronaphthalene (≈70 ml) under Ar was heated at bath temperature of 265 °C with a catalytic amount of ethyl formate (1 ml). Following the evolution of a calculated amount of CO (≈200 cm^3), the reaction mixture was cooled to room temperature, filtered through a pad of silica gel, washed with hexane (removing decahydronaphthalene) and the product was eluted with Et_2O. The solvent was evaporated and the residue purified as described below.

Tricarbonyl[η^6-1,2-di(1,3-dioxolan-2-yl)benzene]chromium (**5**): recrystallization from hexane–ethyl acetate gave 0.76 g (71%) of a yellow crystalline product, m.p. 96–98 °C. IR: 1960, 1875, 1108, 1063. ^{1}H NMR: 4.05–4.17 m, 8 H (OCH_2CH_2O); 5.33–5.36 m, 2 H (Hβ); 5.65–5.68 m, 2 H (Hα); 5.99 s, 2 H (CH). ^{13}C NMR: 66.0, 66.1, 89.8, 91.4, 99.6, 106.3, 232.0. For $C_{15}H_{14}CrO_7$ (358.3) calculated: 50.29% C, 3.94% H; found: 50.39% C, 3.94% H.

Tricarbonyl[η^6-1,3-di(1,3-dioxolan-2-yl)benzene]chromium (**6**): flash chromatography (SiO_2, hexane–ethyl acetate 4:1) and recrystallization from hexane–ethyl acetate afforded 0.77 g (72%) of a yellow crystalline product, m.p. 109–110 °C. IR: 1962, 1877, 1167, 1100. ^{1}H NMR: 4.00–4.18 m, 8 H (OCH_2CH_2O); 5.26 t, 1 H, $^3J_{4,5} = {}^3J_{5,6} = 6.5$ (H5); 5.55 d, 2 H (H4,6); 5.59 s, 2 H (CH); 5.76 s, 1 H (H2). ^{13}C NMR: 66.0, 89.4, 90.1, 91.8, 101.6, 106.0, 231.7. For $C_{15}H_{14}CrO_7$ (358.3) calculated: 50.29% C, 3.94% H; found: 50.21% C, 3.97% H.

Tricarbonyl[η^6-1,4-di(1,3-dioxolan-2-yl)benzene]chromium (**7**): recrystallization from hexane–ethyl acetate afforded 0.77 g (72%) of an orange yellow solid, m.p. 151–153 °C. IR: 1961, 1902, 1882, 1106, 1076. ^{1}H NMR: 4.02–4.13 m, 8 H (OCH_2CH_2O); 5.50 s, 4 H (H-Ar); 5.58 s, 2 H (CH). ^{13}C NMR: 66.0, 89.8, 101.5, 107.8, 231.8. For $C_{15}H_{14}CrO_7$ (358.3) calculated: 50.29% C, 3.94% H; found: 50.21% C, 3.92% H.

Tricarbonyl[η^6-2,2′-di(1,3-dioxolan-2-yl)biphenyl]chromium (**8**): recrystallization from hexane–ethyl acetate furnished 0.81 g (62%) of a yellow crystalline product, m.p. 163–164 °C. IR: 1960, 1873, 1107, 1071. ^{1}H NMR: 3.83–4.13 m, 8 H (OCH_2CH_2O); 5.20 dt, 1 H, $^3J_{3,4} = {}^3J_{4,5} = 6.4$, $^4J_{4,6} = 1.0$ (H4*); 5.31 s, 1 H (CH*); 5.48 dd, 1 H, $^3J_{5,6} = 6.4$ (H6*); 5.57 d, 1 H (H3*); 5.63 dd, 1 H (H5*); 5.72 s, 1 H (CH); 7.38–7.56 m, 4 H (H-Ar). ^{13}C NMR: 65.3, 65.8, 66.0, 66.2, 85.8, 87.7, 94.9, 98.9, 100.3, 101.6, 110.0, 111.9, 126.1, 129.2, 133.6, 133.9, 137.8, 232.3. For $C_{21}H_{18}CrO_7$ (434.4) calculated: 58.07% C, 4.18% H; found: 58.09% C, 4.15% H.

General Procedure for the Preparation of Tricarbonyl(η^6-arenedicarbaldehyde)chromium(0) Complexes by Hydrolysis (**9**–**12**)

A solution of a dioxolane complex (0.28 mmol) in THF (4 ml) was purged with Ar under stirring, and a 50% aqueous H_2SO_4 (2 ml) was added dropwise *via* a syringe at room temperature. The reaction mixture was stirred for 3 h, water (4 ml) was added, and the resultant

mixture was extracted with Et_2O (3 × 10 ml). The organic layer was washed with a saturated Na_2CO_3 solution (10 ml), dried over anhydrous Na_2SO_4 and the solvent evaporated. The residue was purified as described below.

Tricarbonyl(η⁶-phthalaldehyde)chromium (**9**): flash chromatography (SiO_2, hexane–ethyl acetate 4:1) gave 67 mg (88%) of dark-red crystals, m.p. 68 °C (ref.[9] gives m.p. 69 °C). IR: 1976, 1899, 1681, 1172. ^{1}H NMR: 5.65–5.70 m, 2 H (Hβ); 5.87–5.92 m, 2 H (Hα); 10.20 s, 1 H (CHO). ^{13}C NMR: 92.1, 92.4, 96.9, 189.7, 228.6. For $C_{11}H_6CrO_5$ (270.2) calculated: 48.90% C, 2.24% H; found: 48.79% C, 2.12% H.

Tricarbonyl(η⁶-isophthalaldehyde)chromium (**10**): recrystallization from hexane–diethyl ether afforded 56 mg (75%) of red crystals, m.p. 97–98 °C. IR: 1984, 1917, 1688, 1123. ^{1}H NMR: 5.39 t, 1 H, $^3J_{4,5} = {}^3J_{5,6}$ = 6.4 (H5); 6.25 dd, 2 H (H4,6); 6.51 d, 1 H, $^4J_{2,4} = {}^4J_{2,6}$ = 1.2 (H2); 9.55 s, 2 H (CHO). ^{13}C NMR: 87.7, 93.6, 95.1, 95.4, 187.0, 227.0. For $C_{11}H_6CrO_5$ (270.2) calculated: 48.90% C, 2.24% H; found: 48.81% C, 2.22% H.

Tricarbonyl(η⁶-terephthalaldehyde)chromium (**11**): flash chromatography (SiO_2, hexane–ethyl acetate 2:1) and recrystallization from hexane–diethyl ether furnished 60 mg (80%) of red crystals, m.p. 105–107 °C (ref.[10] gives m.p. 107–108 °C). IR: 1982, 1910, 1694, 1207. ^{1}H NMR: 9.94 s, 4 H (H-Ar); 9.65 s, 1 H (CHO). ^{13}C NMR: 91.6, 96.8, 188.6, 228.3. For $C_{11}H_6CrO_5$ (270.2) calculated: 48.90% C, 2.24% H; found: 48.84% C, 2.13% H.

Tricarbonyl(η⁶-biphenyl-2,2′-dicarbaldehyde)chromium (**12**): flash chromatography (SiO_2, hexane–ethyl acetate 5:2) and recrystallization from hexane–diethyl ether gave 51 mg (52%) of a red solid, m.p. 93–95 °C. IR: 1968, 1891, 1691. ^{1}H NMR: 5.36 dd, 1 H, $^3J_{5,6}$ = 6.1, $^4J_{4,6}$ = 1.6 (H6*); 5.60–5.69 m, 2 H (H4,5*); 5.96 dd, 1 H, $^3J_{3,4}$ = 6.0, $^4J_{3,5}$ = 1.7 (H3*); 7.68–7.94 m, 4 H (H-Ar); 9.42 s, 1 H (CHO*); 10.00 s, 1 H (CHO). ^{13}C NMR: 89.5, 91.7, 92.2, 95.5, 96.7, 114.4, 130.1, 132.9, 134.1, 134.4, 134.6, 135.6, 188.3, 191.1, 230.5. For $C_{17}H_{10}CrO_5$ (346.3) calculated: 58.97% C, 2.91% H; found: 58.92% C, 2.85% H.

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