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Resolution of racemic mixtures of chiral arenechromiumtricarbonyl complexes using a Bakerbond Chiralcel HPLC column

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Abstract

Racemic mixtures of eight new chiral arenechromiumtricarbonyl complexes were prepared and fully characterized by IR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. These compounds, along with 25 previously reported chiral complexes were used to establish the ability of commercially available chiral HPLC columns to effect resolution of the mixtures. It was found that Bakerbond Chiralcel OD® columns, consisting of derivatized cellulose on silica gel, successfully resolve racemic mixtures of most arene complexes with good to excellent results. Some tentative patterns in the effect of functional groups and ring substitution on the separation efficiency have been identified and are discussed. Direct resolution of complex **22**, ethyl-*ortho*-methoxybenzoate $Cr(CO)_3$, was performed on the semipreparative scale. The resolved enantiomers were characterized by optical rotation measurements and gave the following data: band 1, $t_{R'1} = 77.8$ min, $[\alpha]_{589}^{21} = +30.0 \pm 4.1°$; band 2, $t_{R'2} = 179.8$ min, $[\alpha]_{589}^{21} = -29.5 \pm 1.0°$.

Keywords: Chromium; Arene complexes; High pressure liquid chromatography; Chirality; Chiral separation; Arenechromiumtricarbonyl

1. Introduction

η^6-Arene and η^5-cyclopentadienyl metal complexes in which the ring is asymmetrically substituted in the 1,2- or 1,3-positions exhibit planar chirality. This property is now being exploited by several groups for the synthesis of complex chiral organic compounds via organometallic intermediates [1,2]. Recognizing that it is not always expedient to convert these chiral complexes into diastereomeric derivatives for resolution, we initiated a program to examine the applicability of commercial HPLC columns using chiral stationary phases for this class of compounds. In this paper, we describe our progress using a very wide range of η^6-arenechromiumtricarbonyl model compounds. We have previously reported an application utilizing HPLC resolution of chiral cyclopentadienyl rhodium complexes [3]. Portions of this work have previously been reported [4].

2. Results and discussion

η^6-Arenechromiumtricarbonyl complexes were prepared by reaction of arenes with chromium hexacarbonyl in refluxing butyl ether:THF solutions according to well established procedures [5]. New compounds were fully characterized by IR, ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis. We have included the previously unreported ^{13}C NMR spectra for several compounds in Section 3. It has been found that carboxaldehyde compounds react with chromium hexacarbonyl under these conditions with substantial decomposition. Conversion of carboxaldehyde groups to their dioxolane derivatives completely inhibits this decomposition pathway.

The chromatographic separation of chiral organometallic compounds was pioneered by Schlögl and his coworkers using triacetylcellulose as a chromatographic solid phase [6]. The use of triacetylcellulose is compli-

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cated by compression of the solid phase bed over time, and the necessity for a small amount of water in the elution solvent. Despite such difficulties, these workers were successful in effecting the resolution of a number of η^6-arenechromiumtricarbonyl compounds on the preparative and semipreparative scale.

Recent advances in chromatography have made available several classes of columns in which the active solid phase is chiral. A survey of the literature on the applicability of these columns suggests that identification of an efficient column material for a given class of compounds remains highly empirical [7]. For this reason we surveyed several column types including "brush type" or Pirkle columns and derivatized cellulose columns. Under our experimental conditions, which typically involve heptane with 10% 2-propanol, we found no evidence for separation of racemic mixtures of either η^6-arenechromiumtricarbonyl or η^5-cyclopentadienylmetalcarbonyl chiral complexes on the Pirkle style columns. In contrast, fair to excellent separations were observed on derivatized cellulose columns.

Derivatized cellulose solid supports were developed by Okamoto and co-workers in Japan and are now available commercially under the trade name of Chiralcel [8]. The Chiralcel series of HPLC columns consists of derivatized cellulose which is adsorbed on macroporous silica. The OD column used in the present work is a 2,5-dimethylphenylcarbamate derivative. We have also found that the related OJ column, in which the benzoyl derivative of cellulose is used as a solid support, is equally effective in resolving racemic mixtures of organometallic materials. An application of the OJ column to semipreparative separations will be reported separately [9].

Table 1 lists the family of η^6-arenechromiumtricarbonyl complexes which have been examined in this work and presents their observed separation efficiencies, α, with their adjusted retention times. Unless

Table 1
Adjusted retention times (min) and selectivity factors (α) for arene chromium tricarbonyl complexes on a Bakerbond CHiralcel OD HPLC column [a]

Compound	$t_{R'1}$	$t_{R'2}$	α
1 Fluorene $Cr(CO)_3$ [10]	75.7	77.5	1.02 [b]
2 9,10-Dihydrophenanthrene $Cr(CO)_3$ [11]	63.7	80.8	1.27
3 10,11-Dihydro-5*H*-di-benzo[a,d]cycloheptane $Cr(CO)_3$ [10]	83.2	96.1	1.16
4 *endo*-9-Methoxyfluorene $Cr(CO)_3$ [12]	83.2	103.6	1.24
5 Indanone $Cr(CO)_3$ [13]	229.8	240.6	1.05 [b]
6 Tetralone $Cr(CO)_3$ [13,14]	98.6	107.4	1.09
7 *endo*-Tetralol $Cr(CO)_3$ [14a]	23.4	31.8	1.36
8 *endo*-Acetyltetralol $Cr(CO)_3$ [12]	60.7	83.2	1.37
9 Dihydrocoumarin $Cr(CO)_3$	38.3	41.6	1.09
10 Isochromanone $Cr(CO)_3$	133.9	145.6	1.09 [c]
11 6-Methoxytetralone $Cr(CO)_3$ [15]	136.9	141.7	1.04 [b]
12 *o*-Methylanisole $Cr(CO)_3$ [16]	26.4	25.2	1.05 [b]
13 *m*-Methylanisole $Cr(CO)_3$ [17]	49.6	73.6	1.48
14 *o*-Toluidine $Cr(CO)_3$ [16,18]	114.0	128.0	1.12 [g]
15 *m*-Toluidine $Cr(CO)_3$ [16]	45.1	64.7	1.43 [b]
16 Ethyl-*o*-toluate $Cr(CO)_3$ [19]		$t_{R'} = 20.7$	1.00 [b,c]
17 Ethyl-*m*-toluate $Cr(CO)_3$ [19]	16.1	19.2	1.19 [f]
18 *o*-Methylacetophenone $Cr(CO)_3$ [20]	66.8	69.7	1.04 [b]
19 *m*-Methylacetophenone $Cr(CO)_3$ [20b-d]	64.0	77.8	1.22
20 *o*-Tolualdehyde $Cr(CO)_3$ [21]		$t_{R'} = 101.5$	1.00 [b]
21 *m*-Tolualdehyde $Cr(CO)_3$ [21a,c]	82.0	127.0	1.55
22 Ethyl-*o*-methoxybenzoate $Cr(CO)_3$	77.8	179.8	2.31
23 Ethyl-*m*-methoxybenzoate $Cr(CO)_3$	43.6	52.6	1.21
24 Ethyl-*o*-methoxyphenylacetate $Cr(CO)_3$	75.6	95.4	1.26
25 Ethyl-*m*-methoxyphenylacetate $Cr(CO)_3$	80.6	178.4	2.21
26 *o*-Anisaldehyde $Cr(CO)_3$ [21b-c,22]	143.5	154.0	1.07
27 *m*-Anisaldehyde $Cr(CO)_3$ [21a,c]	70.9	106.6	1.50
28 *o*-Methylacetophenone-1,3-dioxolane $Cr(CO)_3$	31.8	38.5	1.21
29 *m*-Methylacetophenone-1,3-dioxolane $Cr(CO)_3$	64.7	67.8	1.05 [b,d]
30 *o*-Tolualdehyde-1,3-dioxolane $Cr(CO)_3$ [21a,b]	77.2	165.1	2.14
31 *m*-Tolualdehyde-1,3-dioxolane $Cr(CO)_3$ [21a]		$t_{R'} = 30.4$	1.00 [b]
32 *o*-Anisaldehyde-1,3-dioxolane $Cr(CO)_3$ [21b,22]	258.7	460.9	1.78 [d]
33 *m*-Anisaldehyde-1,3-dioxolane $Cr(CO)_3$ [21a,23]	131.7	136.5	1.04 [b]

[a] Flow rate 0.2 ml min^{-1} unless otherwise noted. Mobile phase consists of heptane/2-propanol (9:1 v/v). [b] Not baseline resolved. [c] Heptane/THF (7:3 v/v). [d] Flow rate 0.1 ml min^{-1}. [e] Flow rate 0.3 ml min^{-1}. [f] Flow rate 0.4 ml min^{-1}. [g] Flow rate 0.5 ml min^{-1}. [h] Flow rate 1.0 ml min^{-1}.

otherwise noted, compounds were separated with baseline resolution. Three of the compounds in the current set were not resolved at all and a fourth was only marginally resolved. Those compounds with α values in excess of 1.2 can be separated on the preparative or semipreparative scale, while those with values between about 1.05 and 1.2 should be separable, albeit with some difficulty.

At the onset of this study it was anticipated that both functional groups and ring substitution positions would effect the efficiency of separation. While some patterns have been observed, there are several exceptions which make it impossible to establish firm rules for the separation efficiency of the columns. An examination of the α values of simple 1,2- and 1,3-disubstituted compounds suggests that the efficiency of separation of 1,3-substituted compounds is generally higher than that of analogous 1,2-compounds. For example, for the series 1-methyl, 2-R, where R = methoxy, carboxaldehyde, ethylcarboxylate, acetyl, and amino, α values are found to range from 1.00 to 1.12. In contrast, the same 1,3-series of compounds has α values in the range 1.19 to 1.55. The substitution of methoxy for methyl on the tolualdehyde ligand has only a small effect on the separation efficiency. Similarly, complexes of ethyl *meta*-toluate (**17**) and ethyl *meta*-methoxybenzoate (**23**) have very similar α values (1.19 and 1.21), while the ethyl *ortho*-toluate (**16**) and ethyl *ortho*-methoxybenzoate (**22**) complexes have dramatically different values ($\approx$ 1.00 and 2.31). In this last instance, the 1,2-disubstituted methoxy compound has a separation efficiency greater than that of its 1,3-analog. We tentatively speculate that an intramolecular interaction between the methoxy methyl group and the ester oxygens alters the contours which this compound presents to the solid support thus enhancing its separation efficiency.

A curious reversal of the separation efficiency pattern is observed for the dioxolane derivatives of acetyl and carboxaldehyde compounds. In these cases, the 1,2-substituted derivatives are found to have higher α values than the 1,3-derivatives.

Complexes which possess bridges between the 1- and 2-positions such as indanone (**5**), tetralone (**6**), isochromanone (**10**), and dihydrocoumarin (**9**) have relatively small separation efficiencies characteristic of 1,2-substitution. Reduction of the ketone in tetralone to an alcohol increases the α value, but the alcohol and its corresponding acetyl derivative have almost identical α values. A series of diarene complexes have been examined. While the fluorene complex (**1**) is barely resolved, observed separations for other members of this family are quite good. Introduction of a methoxy group onto the 9-position of fluorene greatly enhances the separation efficiency.

The significance of this separation technique depends upon its ability to resolve useful amounts of optically pure complexes. We were able to obtain a semipreparative Chiralcel OD column to examine the feasibility of larger scale separations. Under similar conditions employed for the analytical separations, direct resolution of the enantiomers of **22** was performed using the semipreparative column. Complex **22** was chosen for study because of its large selectivity and moderate elution time. The optical rotations of the enantiomers of **22** were: band 1, $t_{R'1} = 77.8$ min, $[\alpha]^{21}_{589} = +30.0 \pm 4.1°$; band 2, $t_{R'2} = 179.8$ min, $[\alpha]^{21}_{589} = -29.5 \pm 1.0°$. The purified enantiomers were then subjected to analytical HPLC analysis and gave the expected single band with correct retention time for each isomer. IR and ^{1}H NMR analysis for each pure enantiomer gave spectra identical to those obtained for the racemate of **22**. Further studies into the relationship between optical rotation, absolute configuration, and elution order are in progress.

Although it appears that prediction of separation efficiency on the basis of functional groups and substitution patterns will not be possible, this technique of direct resolution provides a useful and efficient alternative to conventional methods for resolution of chiral organometallic complexes, and may have important consequences in relation to their use for asymmetric synthesis and catalysis.

3. Experimental details

^{1}H and ^{13}C NMR spectra were recorded on an IBM NR-300 spectrometer and were referenced to the appropriate solvent references. Infrared spectra were recorded on a Bio-Rad Qualimatic FTIR spectrometer. Mass spectrometry was carried out by Dr. Gary Knerr using both electron impact and chemical ionization modes on a VG 7070-HS GC/MS using direct insertion. The optical rotations were performed using a Rudolph Research Instruments polarimeter outfitted with a quartz cell (1 dm length, 1 ml volume) containing ethanol solutions of the chromium complexes. Elemental analyses were conducted by Desert Analytics of Tucson, AZ.

All of the arene ligands were purchased from Aldrich and were used as received. Ethyl esters and 1,3-dioxolanes were prepared by standard literature methods [24]. $Cr(CO)_6$ was purchased from Strem Chemicals, Inc. All solvents were dried and distilled under nitrogen. Preparative chromatography was conducted using nitrogen flushed solvents and neutral (CAMAG) alumina.

Analytical and semipreparative HPLC separations were conducted using a Rainin HPLC pump and plotted using a Spectra-Physics integrating recorder. The columns employed, both analytical (4.6 mm $\times$ 250 mm)

and semipreparative (10 mm × 250 mm), were Chiralcel OD© columns which are commercially available from Daicel Chemical Industries and/or J.T. Baker Co. All separations were conducted under ambient temperature conditions using an isocratic solvent system which was generally composed of heptane/2-propanol (9:1, v/v). The complexes were detected by absorption of UV radiation at 254 nm for the analytical separation. Detection at 280 nm was used for semipreparative separations because there was a tendency for the 254 nm light to cause some decomposition of the complexes as they eluted through the detector chamber. For the semipreparative separations, each enantiomer was collected in flasks wrapped with aluminum foil (for light protection) under nitrogen, then the solvent was removed in vacuo. The flow rate utilized for the resolution of isomers of complex **22** was 4.0 ml min^{-1} (solvent was heptane/2-propanol, 9:1, v/v). After collection, each enantiomer was purified using conventional column chromatography and recrystallization, then the optical rotations were measured using standard procedures [25]. Additionally, IR and ^1H NMR measurements were taken to corroborate the identity of the eluted species.

3.1. General procedure for the synthesis of (η^6-arene) chromium tricarbonyl derivatives

The procedure listed below for the synthesis of ethyl *meta*-methoxybenzoate chromium tricarbonyl, **23**, was used in the preparation of all new compounds.

3.2. Ethyl meta-methoxybenzoate chromium tricarbonyl, 23

$Cr(CO)_6$, 4.4 g (20 mmol), and ethyl 3-methoxybenzoate, 3.3 ml (20 mmol), were taken up in a mixture of butyl ether with 10–15% THF and refluxed for 3 days. The temperature of the reflux for the first 2 days was approximately 70°C and was increased to that of butyl ether (~ 140°C) for the final 24 h period. The reaction mixture was cooled to −78°C for 24 h to precipitate unreacted $Cr(CO)_6$ and then filtered through Celite. The solvent was removed under vacuum from the filtrate to give an orange oil which was chromatographed on neutral alumina using dichloromethane/petroleum ether (1:9). An orange solid, m.p. 31–82°C, was obtained and recrystallized from a mixture of toluene/hexane. Yield: 25.0%. IR: (cm^{-1}, CH_2Cl_2) 1976(s), 1902(s), 1723(m). ^1H NMR: (δ, $CDCl_3$) 5.70(s, 1H, C-2 arene H); 5.58–5.54(m, 2H, arene Hs); 5.27(d, 1H, arene H); 4.39(q, 2H, $-OCH_2CH_3$); 3.74(s, 3H, $-OCH_3$); 1.38(t, 3H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.0(*C*Os); 166.7(*C*(O)OET); 141.6(*ipso*); 93.0, 87.0, 80.2, 77.4(arene *C*s); 62.3($-OCH_2CH_3$); 55.9($-OCH_3$); 14.2($-OCH_2CH_3$) (one *ipso* carbon resonance not observed). MS: 316(M^+), 260(M^+–2CO), 232(M^+–3CO). Anal. Calc. for $C_{13}H_{12}O_6Cr$: C, 49.38; H, 3.82%. Found: C, 49.76; H, 3.85%.

3.3. Ethyl ortho-methoxybenzoate chromium tricarbonyl, 22

IR: (cm^{-1}, CH_2Cl_2) 1977(s), 1903(s), 1726(m). ^1H NMR: (δ, $CDCl_3$) 6.18(d, 1H, arene H); 5.66(t, 1H, arene H); 5.01(d, 1H, arene H); 4.86(t, 1H, arene H); 4.32(q, 2H, $-OCH_2CH_3$); 3.77(s, 3H, $-OCH_3$); 1.32(t, 3H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 231.1(*C*Os); 164.0(*C*(O)OET); 143.7(*ipso*); 96.9, 95.0, 83.6, 72.9(arene *C*s); 82.4(*ipso*); 61.4($-OCH_2CH_3$); 56.0($-CH_3$); 13.9($-OCH_2CH_3$). MS: 316(M^+), 260(M^+–2CO), 232(M^+–3CO). Anal. Calc. for $C_{13}H_{12}O_6Cr$: C, 49.38; H, 3.82%. Found: C, 49.76; H, 3.72%. Orange crystals, m.p. 71–72°C. Yield: 32.9%.

3.4. Ethyl ortho-methoxyphenylacetate chromium tricarbonyl, 24

IR: (cm^{-1}, CH_2Cl_2) 1966(s), 1882(s), 1735(m). ^1H NMR: (δ, $CDCl_3$) 5.57(d, 1H, arene H); 5.48(t, 1H, arene H); 5.07(d, 1H, arene H); 4.91(t, 1H, arene H); 4.15(q, 2H, $-OCH_2CH_3$); 3.78(s, 3H, $-OCH_3$); 3.71(s, 2H, $-CH_2C(O)OET$); 1.26(t, 3H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.9(*C*Os); 170.2(*C*(O)OET); 141.7, 93.2(*ipso* *C*s); 97.2, 93.7, 85.7, 74.2(arene *C*s); 61.2($-OCH_2CH_3$); 56.0($-OCH_3$); 35.1($-CH_2C(O)OET$); 14.1($-OCH_2CH_3$). MS: 330(M^+), 302(M^+–CO), 274(M^+–2CO), 247(M^+–3CO). Anal. Calc. for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27%. Found: C, 50.99; H, 4.34%. Yellow crystals, m.p. 62–63°C. Yield: 42.3%.

3.5. Ethyl meta-methoxyphenylacetate chromium tricarbonyl, 25

IR: (cm^{-1}, CH_2Cl_2) 1966(s), 1887(s), 1735(m). ^1H NMR: (δ, $CDCl_3$) 5.57(t, 1H, C-5 arene H); 5.13(s, 1H, C-2 arene H); 5.08(d, 1H, arene H); 4.85(d, 1H, arene H); 4.18(q, 2H, $-OCH_2CH_3$); 3.72(s, 3H, $-OCH_3$); 3.41(s, 2H, $-CH_2C(O)OET$); 1.28(t, 3H, $-OCH_2CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.9(*C*Os); 169.8(*C*(O)OET); 143.3, 105.9(*ipso* *C*s); 94.7, 86.8, 79.9, 76.7(arene *C*s); 61.5($-OCH_2CH_3$); 55.6($-OCH_3$); 40.5($-CH_2C(O)OET$); 14.1($-OCH_2CH_3$). MS: 330(M^+), 302(M^+–CO), 274(M^+–2CO), 247(M^+–3CO). Anal. Calc. for $C_{14}H_{14}O_6Cr$: C, 50.92; H, 4.27%. Found: C, 51.03; H, 4.29%. Yellow crystals, m.p. 45–46°C. Yield: 21.6%.

*3.6. Isochromanone chromium tricarbonyl, **10***

IR: (cm^{-1}, CH_2Cl_2) 1978(s), 1904(s), 1756(m). ^1H NMR: (δ, $CDCl_3$) 5.46–5.28(m, 5H, arene *H*s and $-CH_2OC(O)CH-$; 4.90(d, 1H, $-CH_2OC(O)CH_2-$); 3.59(dd, 2H, $-CH_2OC(O)CH_2-$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 231.0(*C*Os); 166.3($-CH_2OC(O)CH_2-$); 100.6, 98.9(*ipso C*s); 91.6, 89.9, 89.8, 89.6(arene *C*s); 67.8($-CH_2OC(O)CH_2-$) 34.6($-CH_2OC(O)CH-$). MS: 284(M^+), 228(M^+–2CO), 201(M^+–3CO). Anal. Calc. for $C_{12}H_8O_5Cr$: C, 50.72; H, 2.84%. Found: C, 50.30; H, 2.87%. Yellow crystals, m.p. 132–133°C. Yield: 46.1%.

*3.7. Dihydrocoumarin chromium tricarbonyl, **9***

IR: (cm^{-1}, CH_2Cl_2) 1975(s), 1899(s), 1789(m). ^1H NMR: (δ, C_6D_6) 4.47(d, 1H, arene *H*); 4.32(t, 1H, arene *H*); 4.26(d, 1H, arene *H*); 3.87(t, 1H, arene *H*); 2.30–1.97(m, 2H, $-OC(O)CH_2CH_2-$); 1.64–1.39(m, 2H, $-OC(O)CH_2CH-$). $^{13}C\{^1H\}$ NMR: (δ, C_6D_6) 232.5(*C*Os); 164.2($-OC(O)CH_2CH_2-$); 132.8, 93.0(*ipso C*s); 127.4, 92.7, 86.5, 81.2(arene *C*s); 29.2–OC(O)-CH_2CH_2-; 22.4–DC(O)CH_2CH_2-. MS: Accurate mass; 283.9776 (theoret.), 283.9771(observed), 1.9 ppm error. Nominal mass; 284(M^+), 257(M^+–CO), 229(M^+–2CO), 200(M^+–3CO). Yellow solid, m.p. 140°C dec. Yield: 28.2%.

*3.8. ortho-Methylacetophenone-1.3-dioxolane chromium tricarbonyl, **28***

IR: (cm^{-1}, CH_2Cl_2) 1966(s), 1885(s). ^1H NMR: (δ, $CDCl_3$) 5.94(d, 1H, arene *H*); 5.49(t, 1H, arene *H*); 5.00(t, 1H, arene *H*); 4.94(d, 1H, arene *H*); 4.17–4.02(m, 4H,$-OCH_2CH_2O-$; 2.37(s, 3H, arene-CH_3); 1.61(s, 3H,$-CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 233.3(*C*Os); 112.2($-C[OCH_2CH_2O]CH_3$); 109.4, 107.6(*ipso C*s); 96.4, 94.7, 92.0, 86.9(arene *C*s); 65.2, 65.1($-OCH_2CH_2O-$); 28.5(arene–CH_3); 19.7($-CH_3$) MS: 314(M^+), 258(M^+–2CO), 231(M^+–3CO). Anal. Calc. for $C_{14}H_{14}O_5Cr$: C, 53.51; H, 4.49%. Found: C, 53.84; H, 4.50%. Yellow crystals, m.p. 97–98°C. Yield: 27.7%

*3.9. meta-Methylacetophenone-1.3-dioxolane chromium tricarbonyl, **29***

IR: (cm^{-1}, CH_2Cl_2) 1966(s), 1886(s). ^1H NMR: (δ, $CDCl_3$) 5.53–5.57(m, 4H, arene *H*s); 4.15–4.05(m, 4H, $-OCH_2CH_2O-$); 2.19(s, 3H, arene–CH_3); 1.61(s, 3H, $-CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 233.1(*C*Os); 115.4($-C[OCH_2CH_2O]CH_3$); 106.9, 106.1(*ipso C*s); 94.6, 92.7, 90.7, 89.7(arene *C*s); 65.7 $-OCH_2CH_2O-$; 28.4 (arene–CH_3); 20.7($-CH_3$). MS: 314(M^+), 258(M^+–2 CO), 231(M^+–3CO). Anal. Calc. for $C_{14}H_{14}O_5Cr$: C, 53.51; H, 4.49%. Found: C, 53.54; H, 4.53%. Yellow crystals, m.p. 68–69°C. Yield: 11.6%.

*3.10. ortho-Toluladehyde-1.3-dioxolane chromium tricarbonyl, **30** [21a,b]*

IR: (cm^{-1}, CH_2Cl_2) 1969(s), 1891(s). ^1H NMR: (δ, $CDCl_3$) 5.80(d, 1H, arene *H*); 5.70(s, 1H, $-C[OCH_2-CH_2O]H$); 5.42(*t*, 1H, arene *H*); 5.15(t, 1H, arene *H*); 5.09(d, 1H, arene *H*); 4.16–4.05(m, 4H, $-OCH_2CH_2-O-$), 2.27($-CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.7(*C*Os); 108.9, 104.5(*ipso C*s); 100.0($-C[OCH_2CH_2O]H$); 94.4, 92.9, 92.2, 88.5(arene *C*s); 65.7, 65.5($-OCH_2CH_2O-$), 18.1($-CH_3$). MS: 300(M^+), 244(M^+–2CO), 217(M^+–3CO). Anal. Calc. for $C_{13}H_{12}O_5Cr$: C, 52.01; H, 4.03%. Found: C, 52.12; H, 3.99%. Yellow crystals, m.p. 112–113°C. Yield: 45.6%.

*3.11. meta-Toluladehyde-1.3-dioxolane chromium tricarbonyl, **31** [21a]*

IR: (cm^{-1}, CH_2Cl_2) 1968(s), 1890(s). ^1H NMR: (δ, $CDCl_3$) 5.14(s, 1H); 4.98–4.74(m, 4H); 3.68–3.60(m, 4H, $-OCH_2CH_2O-$) 1.77(s, 3H, $-CH_3$). $^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.7(*C*Os); 128.1, 108.5(*ipso C*s); 101.5($-C[OCH_2CH_2O]H$); 93.0, 92.7, 90.9, 88.0(arene *C*s); 65.6($-OCH_2CH_2O-$); 20.4($-CH_3$). MS: 300(M^+), 244(M^+–2CO), 217(M^+–3CO). Anal. Calc. for $C_{13}H_{12}O_5Cr$: C, 52.01; H, 4.03%. Found: C, 52.30; H, 4.36%. Yellow crystals, m.p. 66–67°C. Yield: 80.7%.

*3.12. 6-Methoxy-1-tetralone chromium tricarbonyl, **11** [15]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 230.9(*C*Os); 195.4($-C(O)CH_2CH_2CH_2-$); 143.9(*ipso*, *C*-6); 115.1, 89.2(*ipso C*s); 91.8, 78.0, 76.5(arene *C*s); 55.8($-OCH_3$); 37.5, 28.5, 21.4($-C(O)CH_2CH_2CH_3-$).

*3.13. meta-Methylacetophenone chromium tricarbonyl, **19** [20b–d]*

^{13}C $\{^1H\}$ NMR: (δ, $CDCl_3$) 231.2(*C*O s); 195.8($-C(O)CH_3$); 106.5, 96.9(*ipso C* s); 95.4, 93.8, 91.7, 90.8(arene *C* s); 25.3(arene-CH_3); 20.6($-C(O)CH_3$).

*3.14. ortho-Tolualdehyde chromium tricarbonyl, **20** [21]*

^{13}C $\{^1H\}$ NMR: (δ, $CDCl_3$) 230.4(*C*O s); 187.5($-C(O)H$); 111.8, 93.5(*ipso C* s); 95.5, 94.8, 91.4, 87.7(arene *C* s); 18.1($-CH_3$).

*3.15. meta-Tolualdehyde chromium tricarbonyl, **21** [21a,c]*

^{13}C $\{^1H\}$ NMR: (δ, $CDCl_3$) 230.6(*C*Os); 188.4($-C(O)H$); 106.1, 95.2(*ipso C*s); 96.0, 94.3, 92.7, 90.3(arene *C*s); 20.5($-CH_3$).

*3.16. ortho-Anisaldehyde chromium tricarbonyl, **26** [21b–c,22]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 230.5(*C*O s); 185.4(–*C*(O)H); 145.7, 86.1(*ipso* *C*s); 94.9, 92.4, 84.3, 72.2(arene *C* s); 56.0(–O*C*H_3).

*3.17. ortho-Anisaldehyde-1,3-dioxolane chromium tricarbonyl, **32** [21b,22]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.4(*C*Os); 142.4(–*C*[OCH_2CH_2O]H); 98.3, 95.3(*ipso* *C*s); 94.4, 93.1, 83.9, 73.0(arene *C* s); 65.7(–OCH_2CH_2O); 56.0(–O*C*H_3).

*3.18. meta-Anisaldehyde chromium tricarbonyl, **27** [21a,c]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 231.0(*C*Os); 189.4(–*C*(O)H); 140.7, 95.8(*ipso* *C*s); 91.8, 89.1, 82.5, 75.6(arene *C*s); 56.2(–O*C*H_3).

*3.19. meta-Anisaldehyde-1.3-dioxolane chromium tricarbonyl, **33** [21a,23]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 232.7(*C*Os); 142.6(–*C*[OCH_2CH_2O]H); 109.6, 101.8(*ipso* *C*s); 93.9, 83.6, 78.1, 75.6(arene *C*s); 65.8(OCH_2CH_2O); 55.7(–O*C*H_3).

*3.20. 1-Indanone chromium tricarbonyl, **5** [13]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 230.1(*C*Os); 202.4(–*C*(O)CH_2CH_2–); 123.2, 95.5(*ipso* *C*s); 96.1, 89.8, 87.0, 80.3(arene *C*s); 34.5, 24.9(–C(O)*C*H_2*C*H_3–).

*3.21. 1-Tetralone chromium tricarbonyl, **6** [13.14]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 230.7(*C*Os); 196.0(–*C*(O)$CH_2CH_2CH_2$–; 115.3, 92.7(*ipso* *C*s); 94.8, 91.2, 89.8, 89.2(arene *C*s); 37.7, 28.3, 21.6(–C(O)*C*H_2*C*H_2-*C*H_3–.

*3.22. 1-Tetralol chromium tricarbonyl, **7** [14a]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 233.3(*C*Os); 113.8, 112.6(*ipso* *C*s); 95.0, 93.3, 90.1, 88.9(arene *C*s); 66.7(–*C*H(OH)$CH_2CH_2CH_2$–; 32.2, 27.6, 19.3(–CH(OH)-*C*H_2*C*H_2*C*H_3–.

*3.23. meta-Toluidine chromium tricarbonyl, **15** [16]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 234.6(*C*Os); 130.2, 111.7(*ipso* *C*s); 96.3, 85.1, 79.8, 75.6(arene *C*s); 21.0–*C*H_3).

*3.24. Ethyl-ortho-toluate chromium tricarbonyl, **16** [19]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 231.3(*C*Os); 165.8(–*C*(O)OET); 111.9, 93.0(*ipso* *C*s); 96.6, 95.3, 92.3, 87.6(arene *C*s); 61.7(C(O)OCH_2CH_3); 21.2(arene-*C*H_3); 14.2(–C(O)OCH_2*C*H_3).

*3.25. Ethyl meta-toluate chromium tricarbonyl, **17** [19]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$) 231.6(*C*Os); 165.8(–*C*(O)OET); 106.8, 91.5(*ipso* *C*s); 94.6, 94.1, 91.7, 91.3(arene *C*s); 62.0(C(O)OCH_2CH_3); 20.6(arene-*C*H_3); 14.2(–C(O)OCH_2*C*H_3).

*3.26. ortho-Methylanisole chromium tricarbonyl, **12** [16]*

$^{13}C\{^1H\}$ NMR: (δ, $CDCl_3$3)233.7(*C*Os); 141.4, 98.3(*ipso* *C*s); 97.0, 92.7, 86.4, 75.0(arene *C*s); 55.8(–O*C*H_3); 16.0(arene-*C*H_3).

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