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On the Deprotonation of η^6-1,3-Dimethoxybenzene-$Cr(CO)_3$ Derivatives: Influence of the Reaction Conditions on the Regioselectivity

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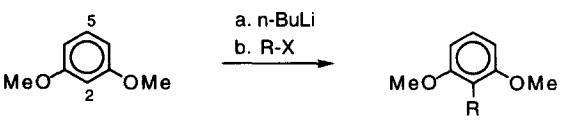
Abstract: The regioselectivity of deprotonation / alkylation reactions of η^6-1,3-dimethoxybenzene-$Cr(CO)_3$ (**5**), η^6-1,3-dimethoxy-5-methylbenzene-$Cr(CO)_3$ (**6**) and 2-substituted derivatives of these compounds was investigated. It is shown that the regioselectivity highly depends on the reaction conditions. For instance, deprotonation of η^6-1,3-dimethoxy-2-(trimethylsilyl)benzene-$Cr(CO)_3$ (**10**) with *n*-BuLi followed by silylation or methylation affords 4-substituted products while the use of LiTMP at -78 °C cleanly gives rise to 5-substituted products. The regioselective alkylation of complexes of type **6** at the 5-methyl group is easily achieved. The usefulness of the latter possibility is demonstrated in a synthesis of olivetol dimethyl ether (**33**). © 1997 Elsevier Science Ltd.

Introduction

The use of arene-$Cr(CO)_3$ complexes in organic synthesis has been a field of growing importance in recent years.[1] Among the variety of reactivity patterns common to arene-$Cr(CO)_3$ complexes, the facilitated deprotonation of arylic[2] and benzylic[3] positions has often been exploited in the course of total syntheses to obtain functionalized aromatic intermediates with excellent yields. In the course of our own research directed towards the synthetic application of arene-$Cr(CO)_3$ complexes,[4] we became interested in the preparation of 5-substituted and 2,5-disubstituted resorcinol derivatives, as these substructures occur in a number of interesting bioactive natural products[5] including some recently discovered DNA cleaving agents isolated from australian *Hakea* plants,[6] or resveratrol, a potential anticancer compound found in grapes and other fruits.[7]

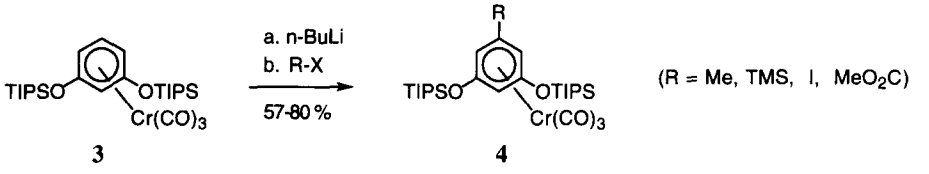
The common strategies aimed at the synthesis of 5-substituted resorcinol derivatives are either based on the construction of the aromatic ring[8] or on the use of (expensive) 3,5-dimethoxybenzaldehyde as the starting material.[9] Due to the *ortho*-directing effect of methoxy groups in the metallation of aromatic compounds,[10] 2-alkyl resorcinols (of type **2**) can, in general, be easily prepared *via* lithiation of (inexpensive) resorcinol dimethyl ether (**1**) with *n*-butyllithium followed by alkylation as depicted in Scheme 1.[11] Nevertheless, the regioselective alkylation of **1** (or **2**) in 5-position is not possible by common methodology.



1 **2**

Scheme 1

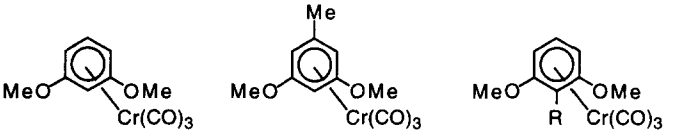
Several authors have shown that alkoxy-substituted arene $Cr(CO)_3$-complexes can be subjected to directed *ortho*-metallations, too, providing *ortho*-alkylated products under even milder conditions.[12,13] As an important further development, Widdowson demonstrated that the regioselective *meta*-lithiation of complexed phenol derivatives is possible when the sterically more encumbered triisopropylsilyl (TIPS-) ethers are employed.[14] Accordingly, the di-O-silylated resorcinol complex **3** is selectively lithiated by *n*-butyllithium in 5-position giving access to a variety of substituted complexes of type **4** in good yield (Scheme 2).[15] However, the toll for the high 5-regioselectivity is quite high. If the products (**4**) have, for instance, to be further functionalized in 2-position, the (expensive) TIPS groups must be exchanged against methyl groups as it was demonstrated by Widdowson in his synthesis of moracin C.[16]



3 **4**

Scheme 2

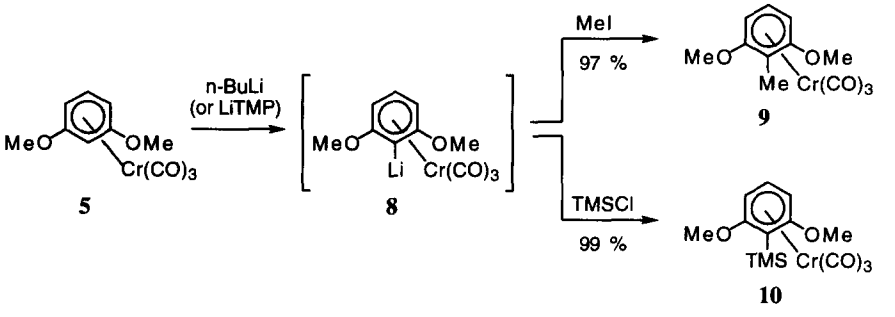
We here report on deprotonation / alkylation experiments employing the (easily available) resorcinol dimethyl ether complex **5**,[17] the orcinol dimethyl ether complex **6** and 2-substitued derivatives thereof. We demonstrate that the regioselectivity is highly dependent on the reaction conditions and, even more importantly, that a direct regioselective 5-functionalization of complexes of type **7** is possible.



5 **6** **7**

Results and Discussion

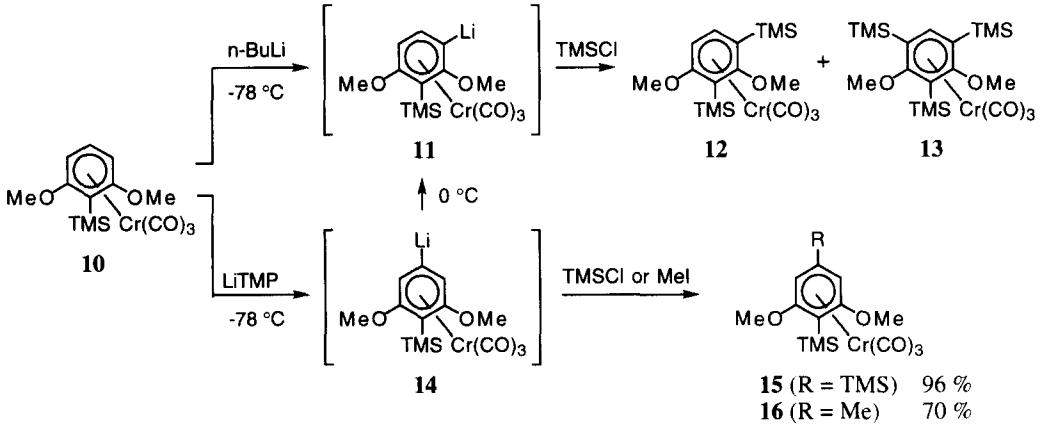
When **5**, prepared by complexation of resorcinol dimethyl ether **1** under standard conditions,[18] was deprotonated with *n*-butyllithium in THF (→ intermediate **8**) followed by alkylation (or silylation), the 2-substituted compounds **9** and **10**, respectively, were regioselectively obtained in excellent yield (Scheme 3).



5 **8** **9** **10**

Scheme 3

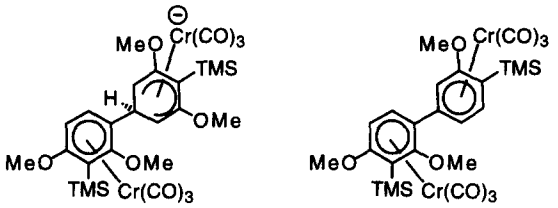
The deprotonation of **10** with *n*-butyllithium in THF (-78 °C) occured selectively *ortho* to a methoxy group, as expected. On addition of chlorotrimethylsilane (TMSCl) to the solution of the lithiated intermediate (*rac*-**11**), the silylation product *rac*-**12** was formed in 25-58 % yield together with varying amounts (9-30 %) of the trisilylated compound **13** and starting material (Scheme 4). The highest yields of *rac*-**12** were obtained when the TMSCl was added rapidly or by inverse addition. *In contrast, when* **10** *was treated with 1-lithio-2,2,6,6-tetramethylpiperidide (LiTMP) at -78 °C followed by silylation or methylation, the 5-substituted compounds* **15** *or* **16**, *respectively, were obtained in excellent yield with complete regioselectivity .*



Scheme 4[19]

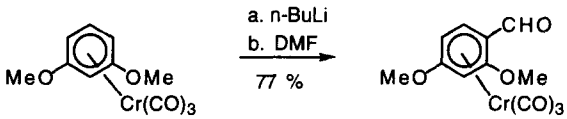
We believe that both intermediates (*rac*-**11** and **14**) are formed kinetically controlled from **10** under the conditions given above. Intermediate *rac*-**11** is the product of a directed *ortho*-metallation[10] while **14** is formed under the action of a sterically hindered base. This picture is supported by the fact, that the use of lithiumdiisopropylamide (LDA) at -78 °C followed by silylation also afforded the 5-silylated product **15** (50 % isolated yield). Also, when LiTMP was added to a THF solution of **10** at 0 °C in the presence of TMSCl (*in situ quench conditions*),[20] only **15** was formed (77 % isolated yield). On the other hand, deprotonation of **10** with *n*-butyllithium in the presence of TMEDA at -78 °C followed by fast addition of TMSCl gave rise to the almost pure isomer *rac*-**12** (58 % isolated yield). Interestingly, on treatment of **10** with LiTMP at 0 °C followed by addition of TMSCl, the 5-substituted compound (**15**) was not formed at all. In this case, *rac*-**12** was obtained as the sole regioisomer. This indicates that equilibration of the initially formed intermediate **14** to *rac*-**11** occurs under these conditions prior to silylation (thermodynamic control). To probe whether the use of LiTMP would even allow the direct alkylation of **5** in 5-position, a solution of this substrate was slowly added to a LiTMP solution at - 78 °C followed by the addition of methyl iodide. In this case, however, compound **9** was exclusively obtained in high yield (95 %). This demonstrates the steric effect being not strong enough to overcompensate the much higher acidity of the double activated proton in position 2.

Strangely enough, treatment of **10** with *n*-butyllithium in the presence of TMEDA at - 20 °C followed by addition of TMSCl at 0 °C did neither yield *rac*-**12** nor **15**, but provided the biphenyl derivative *rac*-**18**[21] in 85 % yield. This unexpected reaction outcome (*tele*-substitution of a OMe group)[22] can be understood assuming a nucleophilic attack of the deprotonated species *rac*-**11** at the 5-position of **10** giving rise to an intermediate of type *rac*-**17**, which on protic workup eliminates methanol according to the mechanism of Rose.[23]



17 **18**

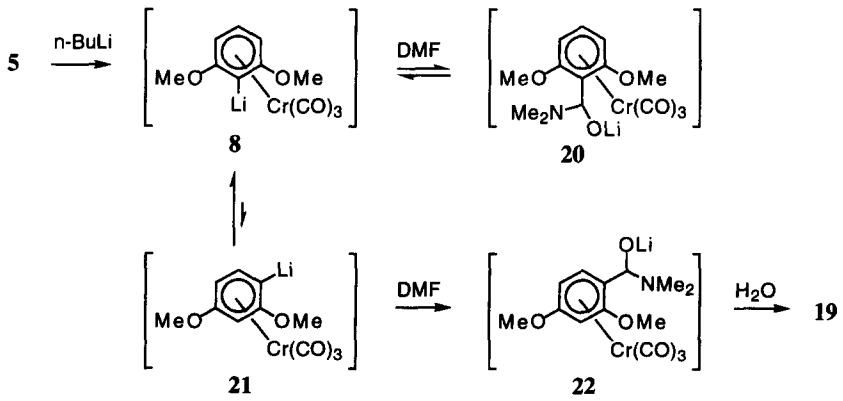
Another unexpected product was observed in the following experiment. Deprotonation of **5** with *n*-butyllithium (1 equiv.) in THF at -78 °C followed by addition of DMF (2.5 equiv., -78 to 0 °C, 1 h) and hydrolytic workup did not yield any of the 2-substituted product. Instead, the 4-formylated compound *rac*-**19** was obtained in 77 % yield (Scheme 5), which could be easily identified from the splitting pattern of the aromatic ^{1}H NMR signals. This result is rather remarkable since the earlier alkylation experiments (Scheme 3) had established that the (expected) intermediate **8** is formed on deprotonation of **5**. An attempt to achieve the formylation of **5** in 2-position by transferring a solution of the lithiated intermediate (**8**) to an excess of DMF (reverse addition) also furnished *rac*-**19** as the major product (63 % isolated yield). Nevertheless, the expected 2-formylated product (**7**, R = CHO) could be isolated at least in 4 % yield in this case.



5 **19**

Scheme 5[19]

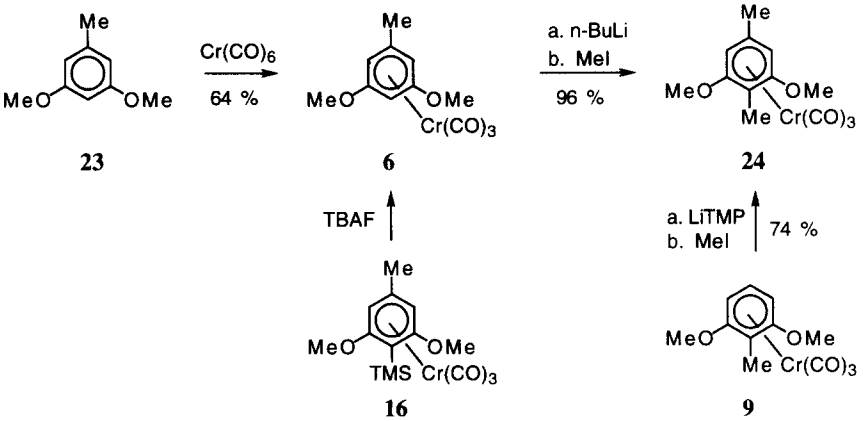
To explain the unexpected selectivity in the formylation of **5**, we assume the reaction of the intermediate **8** with DMF (→ **20**) being reversible or slow under the reaction conditions. In addition, we speculate that **8** may equilibrate to *rac*-**21** which is trapped by DMF in a fast and irreversible manner to furnish *rac*-**22** from which *rac*-**19** would finally be obtained by hydrolysis (Scheme 6).[24]



8 **20** **21** **22**

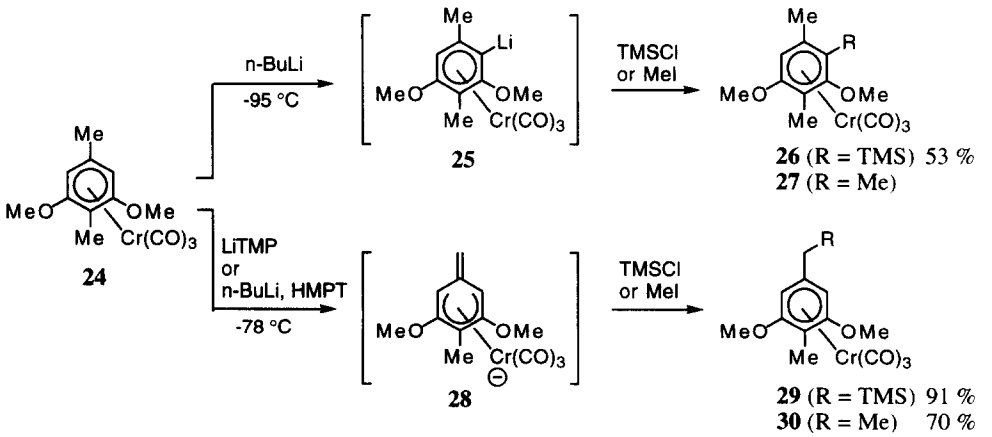
Scheme 6[19]

In a second set of experiments, we investigated the deprotonation of 5-methylated compounds such as **16** or **24**. The latter was obtained in high yield by alkylation of complex **6**, obtained either from orcinol dimethyl ether (**23**)[25] by complexation or from **16** by desilylation. Alternatively, **24** could also be prepared from **9** by regioselective 5-methylation at -78 °C employing LiTMP as base (Scheme 7).



Scheme 7

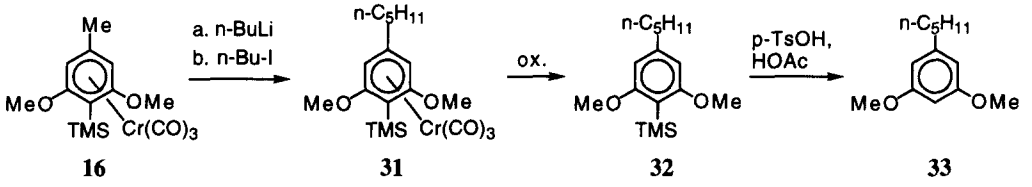
Deprotonation of **24** with *n*-butyllithium in THF at very low temperatures occurs preferentially at the ring to give intermediate *rac*-**25** as it is evidenced by the formation of *rac*-**26** or *rac*-**27** as the major products after addition of TMSCl or methyl iodide, respectively (Scheme 8). As by-products the isomeric compounds **29** and **30**, respectively, are observed even at -95 °C and in increasing amounts at higher temperatures. Interestingly, deprotonation of **24** under a variety of other conditions (e.g. LiTMP, -78 °C; *s*-BuLi, -78 °C, *n*-BuLi, HMPA, -78 °C) takes place regioselectively in benzylic position (at the methyl group in 5-position) to give the thermodynamically more stable intermediate **28** (red solution), from which the symmetrically substituted complexes **29** or **30**, respectively, are selectively obtained in high yield after addition of TMSCl or methyl iodide (Scheme 8).



Scheme 8[19]

The regioselectivity of the benzylic deprotonation of **24** was unambiguously proven by NOE measurements of the silylation product **29** thus confirming that proton abstraction (from **24**) takes place at the less deactivated methyl group *meta* to the methoxy groups (electronic control). The desilylation of **29** to **24** was easily achieved in 94 % yield by treatment of **29** with tetrabutylammonium fluoride (THF, H_2O, 25 °C, 30 min).

The synthetic value of the chemistry described above was demonstrated in a five-step synthesis of olivetol dimethyl ether (**33**)[26] (Scheme 9). Starting from resorcinol dimethyl ether (**1**), complex **16** was prepared in three steps as described above. Benzylic deprotonation / butylation of **16** resulted in the formation of complex **31** which was usually directly oxidatively decomplexed to afford **32** in 57 % overall yield from **16**. Protodesilylation of **32** then furnished the known olivetol precursor **33** in 82 % yield.[27]



Scheme 9

Conclusion

Our results demonstrate for the case of several 1,3-dimethoxybenzene derivatives that the regioselectivity of the deprotonation of arene-$Cr(CO)_3$ complexes can be highly dependent on the reaction conditions.[28] The most striking result is that the *ortho*-directing influence of a methoxy substituent can be overcompensated by use of a sterically demanding base allowing a (contra-thermodynamic) selective functionalization in 5-position. Furthermore, the deprotonation of **16** or **24** occurs with surprising ease in benzylic position (at the methyl group at C-5). As illustrated by the synthesis of olivetol dimethyl ether we believe that our findings represent a synthetically important extension of arene-$Cr(CO)_3$ chemistry.

EXPERIMENTAL

General Methods: Manipulations involving air sensitive compounds were carried out in an argon atmosphere using Schlenk and syringe techniques. Melting points are uncorrected. FT-IR spectra were recorded with a *Nicolet* Magna FT-IR spectrometer usually using the ATR (attenuated total reflectance) technique. Wavenumbers are quoted in cm^{-1}, abbreviations are: s, strong; m, medium; w, weak and br, broad. NMR spectra were recorded on *Bruker* AM 250, AM 270 or AM 400 spectrometers. All NMR recordings were referenced to the $CHCl_3$ resonances (7.26 and 77.0 ppm). ^1H NMR: splitting patterns abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; ψ, pseudo. ^{13}C NMR: multiplicities were determined by DEPT, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. High resolution mass spectra (HRMS) were obtained with a *Varian* MAT 711 instrument (70 eV). Elemental analyses were performed on a *Perkin-Elmer* CHNO/S-Analysator 2400 II or a *Heraeus* CHN-Rapid instrument. Analytical thin layer chromatography (TLC) was performed using *Merck* Silica 60 F 254 glass plates; the chromatograms were visualized under ultraviolet light and/or by staining with a cerium reagent (prepared by dissolving 2 g of phosphomolybdic acid, 1g

cerium(IV)sulfate and 10 ml conc. sulfuric acid in 90 ml H_2O) followed by heating. Flash chromatography[29] was performed using *Merck* Silica 60 (230 - 400 mesh). Preparative thin layer chromatography (PTLC) was carried out using a chromatotron (*Harrison Research* Model 7924 T) on glass plates coated with 1 - 4 mm layers of silica gel containing gypsum (*Merck* PF 60 F 254). Anhydrous THF was freshly distilled from sodium/benzophenone in an argon atmosphere. Methyl *tert.*-butyl ether is abbreviated as MTBE.

Tricarbonyl-[η^6-1,3-dimethoxy-benzene]-chromium(0) (**5**). A dry 100 ml Schlenk flask equipped with a reflux condenser and a Hg-bubbler was charged with a mixture of 1,3-dimethoxybenzene (**1**) (1.38 g, 10 mmol), $Cr(CO)_6$ (3.3 g, 15 mmol) and 80 ml of *n*-Bu_2O. The whole apparatus was evacuated and flushed with argon several times. Then 8 ml of dry THF were added with a syringe and the mixture was heated to reflux for 18 h. The still warm (ca. 40 °C) reaction mixture was filtered through a short pad of silica under argon and the solvents were removed in vacuo. The residue was crystallized from hexane/EtOAc = 10:1 to yield 1.38 g (50 %) of **5** as yellow prisms; mp.: 139 °C (ref.[17]: 122 °C); TLC (hexane/EtOAc = 10:1); IR (ATR): 3101 (w), 2984 (w), 2941 (w), 1951 (m), 1847 (s), 1545 (m), 1468 (w), 1210 (m), 1149 (m), 678 (w); ^{1}H NMR (400 MHz): δ = 3.76 (s, 6 H), 4.84 (dd, 2 H, J_1 = 1.9 Hz, J_2 = 6.8 Hz), 5.19 (t, 1 H, J = 1.9 Hz), 5.61 (t, 1 H, J = 6.8 Hz); ^{13}C NMR (67 MHz): δ = 55.7 (q), 69.3 (d), 72.8 (d), 93.2 (d), 143.8 (s), 233.5 (s); MS (m/z) = 274 (M^+, 23), 218 (9), 190 (67), 57 (100), 56 (97); HRMS calcd. for $C_{11}H_{10}O_5Cr$: 273.9933; found: 273.9944. Anal. Calcd. for $C_{11}H_{10}O_5Cr$: C, 48.18, H, 3.68; found: C, 48.15, H, 3.68.

Tricarbonyl-[η^6-1,3-dimethoxy-2-methyl-benzene]-chromium(0) (**9**). *Procedure A*: A stirred solution of 100 mg (0.36 mmol) of **5** in 2.5 ml of dry THF was cooled to -78 °C and 0.25 ml (0.4 mmol) of *n*-BuLi (1.6 M in hexane) were injected. After 15 min 0.056 ml (0.9 mmol) of MeI were added and stirring was continued at -78 °C for 15 min and at 0 °C for 1 h. The mixture was then diluted with 50 ml of EtOAc, washed with H_2O (2x30 ml) and brine (2x30 ml) and dried over Na_2SO_4. The solvent was removed in vacuo to yield 101 mg (97 %) of essentially pure **9**. *Procedure B*: A stirred solution of 0.34 ml (2 mmol) of 2,2,6,6- tetramethylpiperidine in 3 ml of dry THF was cooled to -78 °C and 1.25 ml (2 mmol) of *n*-BuLi (1.6 M in hexane) were added slowly. After stirring for 15 min (-78 → -40 °C) the stirred solution was recooled to -78 °C and a solution of **5** (500 mg, 1.8 mmol) in 3 ml of dry THF was added dropwise. After 1 h at -60 °C, this solution was slowly transferred by means of a transfer needle to a cold (-60 °C), stirred solution of 0.57 ml (9.1 mmol) of MeI in 6 ml of dry THF. After 30 min at -60 °C the mixture was allowed to warm to room temperature (1 h). The mixture was then diluted with 50 ml of EtOAc, washed with sat. aqueous $NaHCO_3$ (2x80 ml) and brine (2x80 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow crystalline residue was recrystallized from hexane/EtOAc to yield 501 mg (95 %) of **9** as pale yellow crystals; mp.: 99 °C; TLC (hexane/EtOAc = 5:1); IR (ATR): 3120 (w), 2980 (w), 2943 (w), 1942 (s), 1869 (m), 1844 (m), 1834 (s), 1536 (w), 1462 (w), 1286 (w), 1250 (w), 1122 (m), 668 (w); ^{1}H NMR (400 MHz): δ = 2.13 (s, 3 H), 3.82 (s, 6 H), 4.85 (d, 2 H, J = 6.5 Hz), 5.51 (t, 1 H, J = 6.8 Hz); ^{13}C NMR (100 MHz): δ = 9.4 (q), 55.9 (q), 70.2 (d), 88.8 (s), 91.4 (d), 143.1 (s), 234.2 (s); MS (m/z) = 346 (M^+, 15), 334 (57), 290 (10), 262 (100), 217 (9), 190 (11), 135 (9), 52 (26); HRMS calcd. for $C_{12}H_{12}O_5Cr$: 288.0090; found: 288.0088. Anal. Calcd. for $C_{12}H_{12}O_5Cr$: C, 50.01, H, 4.20; found: C, 50.20, H, 4.28.

Tricarbonyl-[η^6-1,3-dimethoxy-2-trimethylsilyl-benzene]-chromium(0) (**10**). A solution of **5** (392 mg, 1.4 mmol) in 10 ml of dry THF was cooled to -78 °C before 0.9 ml (1.44 mmol) of *n*-BuLi (1.6 M in *n*-hexane) were added. After stirring for 30 min, 0.443 ml (3.5 mmol) of TMSCl were injected, the cooling bath was removed and the mixture was allowed to stir at room temperature for 1 h. The mixture was then diluted with

50 ml of EtOAc, washed with sat. aqueous $NaHCO_3$ (2x50 ml) and brine (2x50 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue was crystallized from hexane to yield 485 mg (99 %) of **10**; mp.: 151 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2975 (w), 2957 (w), 2903 (w), 1943 (s), 1871 (s), 1843 (s), 1524 (m), 1505 (m), 1453 (s), 1442 (s), 1415 (m), 1285 (m), 1238 (s), 1096 (s), 847 (s), 669 (m); ^{1}H NMR (400 MHz): δ = 0.34 (s, 9 H), 3.68 (s, 6 H), 4.71 (d, 2 H, J = 6.8 Hz), 5.72 (t, 1 H, J = 6.8 Hz); ^{13}C NMR (100 MHz): δ = 1.6 (q), 55.4 (q), 69.7 (d), 93.2 (d), 148.4 (s), 234.2 (s); MS (m/z) = 346 (M^+, 15), 334 (57), 290 (10), 262 (100), 217 (9), 190 (11), 135 (9), 52 (26); HRMS calcd. for $C_{14}H_{18}O_5CrSi$: 346.0329; found: 346.0336. Anal. Calcd. for $C_{14}H_{18}O_5CrSi$: C, 48.55, H, 5.24; found: C, 48.58, H, 5.28.

Tricarbonyl-[η^6-1,3-dimethoxy-2,4-bis(trimethylsilyl)-benzene]-chromium(0) (*rac*-**12**). A stirred solution of **10** (50 mg, 0.14 mmol) in 2 ml of dry THF and 0.05 ml of TMEDA was cooled to -78 °C and 0.1 ml (0.16 mmol) of *n*-BuLi (1.6 M in hexane) were added. After stirring for 30 min at the same temperature, 0.09 ml (0.72 mmol) of TMSCl were injected all at once and stirring was continued for 1.5 h (-78 °C → 0 °C). The mixture was diluted with 20 ml of EtOAc, washed with sat. aqueous $NaHCO_3$ (2x50 ml) and brine (2x50 ml) and dried over Na_2SO_4. TLC indicated the formation of one major new product (*rac*-**12**) besides small amounts of a (less polar) by-product (**13**) and some starting material (**10**). The solvent was removed in vacuo and the yellow oil was purified by PTLC using hexane/EtOAc = 5:1 to yield 35 mg (58 %) of *rac*-**12**; mp.: 129 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2955 (w), 2900 (w), 2847 (w), 1954 (s), 1875 (s), 1499 (m), 1313 (m), 1268 (m), 1251 (m), 1112 (m), 842 (s), 664 (m); ^{1}H NMR (400 MHz): δ = 0.35 (s, 9 H), 0.44 (s, 9 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 4.77 (d, 1 H, J = 3 Hz), 5.69 (d, 1 H, J = 3 Hz); ^{13}C NMR (100 MHz): δ = 0.3 (q), 1.8 (q), 55.5 (q), 64.2 (q), 72.2 (d), 77.4 (s), 87.9 (s), 99.0 (d), 149.4 (s), 234.1 (s); MS (m/z) = 418 (M^+, 23), 406 (42), 362 (14), 334 (100), 319 (9), 237 (11), 207 (22), 73 (12), 52 (12). HRMS calcd. for $C_{17}H_{26}O_5CrSi_2$: 418.0724; found: 418.0732.

Tricarbonyl-[η^6-1,3-dimethoxy-2,4,6-tris(trimethylsilyl)-benzene]-chromium(0) (**13**). A stirred solution of **10** (100 mg, 0.29 mmol) in 2 ml of dry THF was cooled to -78 °C and 0.17 ml (0.27 mmol) of *n*-BuLi (1.6 M in hexane) were added. After 30 min, 0.120 ml (0.86 mmol) of TMSCl were added dropwise and stirring was continued for 1 hour at -78 °C and 30 min at 0 °C. The mixture was diluted with 20 ml of EtOAc, washed with sat. aqueous $NaHCO_3$ (2x50 ml) and brine (2x50 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oil was purified by PTLC using hexane/EtOAc = 10:1 to yield 42 mg (30 %) of **13** together with 30 mg of *rac*-**12** (25 %) and 23 mg (23 %) of reisolated starting material (**10**). Data for **13**: mp.: 220 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2953 (w), 2902 (w), 2847 (w), 1946 (s), 1885 (s), 1871 (s), 1342 (m), 1293 (m), 1250 (m), 1004 (m), 840 (s), 671 (m); ^{1}H NMR (400 MHz): δ = 0.37 (s, 18 H), 0.51 (s, 9 H), 3.75 (s, 6 H), 5.63 (s, 2 H); ^{13}C NMR (100 MHz): δ = 0.3 (q), 2.7 (q), 63.9 (q), 87.6 (s), 90.3 (s), 105.0 (d), 154.3 (s), 233.9 (s); MS (m/z) = 490 (M^+, 8), 406 (100), 334 (9), 172 (50), 145 (27), 116 (21), 104 (60), 91 (45), HRMS calcd. for $C_{20}H_{34}O_5CrSi_3$: 490.1119; found: 490.1111. Anal. Calcd. for $C_{20}H_{34}O_5CrSi_3$: C, 48.95, H, 6.98; found: C, 48.52, H, 7.01.

Tricarbonyl-[η^6-1,3-dimethoxy-2,5-bis(trimethylsilyl)-benzene]-chromium(0) (**15**). A stirred solution of 50 mg (0.15 mmol) of **10** and 0.090 ml (0.72 mmol) of TMSCl in 10 ml of dry THF was cooled to -78 °C. In a separate flask, a solution of 0.06 ml (0.36 mmol) of 2,2,6,6-tetramethylpiperidine in 5 ml of dry THF was cooled to -40 °C and 0.23 ml (0.36 mmol) of *n*-BuLi (1.6 M in hexane) were injected. After 5 min, this solution was slowly added to the contents of the first flask by means of a transfer canula and the cooling bath was removed. The solution was allowed to stir at room temperature for 1 h. After addition of 50 ml of EtOAc the mixture was washed with 2 N HCl (2x50 ml), sat. aqueous $NaHCO_3$ (2x50 ml) and brine (2x50 ml) and dried

over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue was purified by PTLC (hexane/EtOAc = 10:1) to yield 60 mg (96 %) of **15** as yellow crystals; mp.: 154 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2979 (w), 2955 (w), 2900 (w), 2845 (w), 1936 (s), 1876 (s), 1851 (s), 1521 (w), 1479 (s), 1292 (m), 1230 (s), 1110 (s), 844 (s), 670 (m); ^{1}H NMR (400 MHz): δ = 0.37 (s, 9 H), 0.38 (s, 9 H), 3.69 (s, 6 H), 4.54 (s, 2 H); ^{13}C NMR (67 MHz): δ = -1.6 (q), 1.5 (q), 55.2 (q), 72.8 (d), 77.2 (s), 100.9 (s), 149.2 (s), 234.3 (s); MS (m/z) = 418 (M^+, 9), 362 (8), 334 (100), 207 (24), 172 (38), 145 (25), 116 (16), 104 (45), 28 (45). HRMS calcd. for $C_{17}H_{26}O_5CrSi_2$: 418.0724; found: 418.0724. Anal. Calcd. for $C_{17}H_{26}O_5CrSi_2$: C, 48.78, H, 6.26; found: C, 48.51, H, 6.29.

Tricarbonyl-[η^6-1,3-dimethoxy-5-methyl-2-(trimethylsilyl)-benzene]-chromium(0) (**16**). To a stirred solution of 2,2,6,6-tetramethylpiperidine (0.276 ml, 1.6 mmol) in 5 ml of dry THF was added at -78 °C 1 ml (1.6 mmol) of *n*-BuLi (1.6 M in hexane). After 15 min, a solution of 500 mg (1.44 mmol) of **10** in 2 ml THF was slowly injected and stirring was continued for 30 min before the mixture was slowly transferred with a canula to a solution of 0.45 ml of MeI in 20 ml of THF cooled to -50 °C. After 30 min the cooling bath was removed and stirring continued for 1 h at room temperature. The mixture was diluted with 50 ml of *n*-heptane and ca. 50 % of the solvent was removed under reduced pressure. 50 ml of EtOAc were then added and the yellow solution was washed with 2 N HCl (2x100 ml), sat. aqueous $NaHCO_3$ (2x100 ml) and brine (2x100 ml) and dried over Na_2SO_4. The solvent was finally removed in vacuo to yield 370 mg (70 %) of **16**; mp.: 158 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2950 (w), 2901 (w), 1937 (s), 1863 (s), 1849 (s), 1320 (w) 1229 (m), 1112 (w), 839 (w); ^{1}H NMR (400 MHz): δ = 0.33 (s, 9 H), 2.35 (s, 3 H), 3.68 (s, 6 H), 4.65 (s, 2 H); ^{13}C NMR (67 MHz): δ = 1.5 (q), 21.3 (q), 55.3 (q), 72.6 (d), 77.2 (s), 108.4 (s), 148.2 (s), 234.6 (s); MS (m/z) = 217 (42), 161 (63), 144 (16), 102 (61), 88 (29), 57 (100); HRMS calcd. for $C_{15}H_{20}O_5CrSi$: 360.0485; found: 360.0488. Anal. Calcd. for $C_{15}H_{20}O_5CrSi$: C, 49.99, H, 5.60; found: C, 50.24, H, 5.67.

*Formation of the biphenyl derivative rac-***18**. A solution of 100 mg (0.29 mmol) of **10** in 2 ml of dry THF was cooled to -20 °C and 0.096 ml of TMEDA and 0.170 ml (0.27 mmol) of *n*-BuLi (1.6 M in hexane) were added slowly. Stirring was continued at 0 °C for 1 h before 0.120 ml (0.86 mmol) of TMSCl were added. After 1 h stirring (0 °C → room temperature), the mixture was diluted with 50 ml of EtOAc, washed with 2 N HCl (2x50 ml), sat. aqueous $NaHCO_3$ (2x50 ml) and brine (2x50 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue was purified by PTLC (hexane/EtOAc = 10:1) to yield 81 mg (85 %) of an unseparable mixture consisting majorly of *rac*-**18** (or its diastereomer). mp.: 182 °C (decomposition); TLC (hexane/EtOAc = 10:1); IR (ATR): 2956 (w), 2899 (w), 2845 (w), 1952 (s), 1879 (s), 1532 (w), 1497 (w), 1462 (w), 1406 (w), 1382 (w), 1326 (w), 1272 (w), 1221 (w), 1207 (w), 1178 (w), 1161 (w), 1085 (w), 1067 (w), 1022 (w), 1004 (w), 917 (w), 843 (m), 766 (w), 664 (w); ^{1}H NMR (400 MHz; only the signals of the major component are given): δ = 0.32 (s, 9 H), 0.40 (s, 9 H), 3.55 (s, 3 H), 3.75 (s, 3 H), 3.84 (s, 3 H), 4.96 (d, 1 H, J = 2.5 Hz), 5.19 (d, 1 H, J = 2.5 Hz), 4.52 (s, 1 H), 5.6 (d, 1 H, J = 2.5 Hz), 6.28 (d, 1 H, J = 2.5 Hz); ^{13}C NMR (100 MHz; only the signals of the major component are given): δ = -0.7 (q), 1.6 (q), 55.6 (q), 55.7 (q), 63.9 (q), 70,1 (d), 78.6 (d), 88.0 (s), 88.1 (d), 93.9 (s), 98.0 (d), 99.2 (d), 109.6 (s), 146.1 (s), 147.3 (s), 147.5 (s), 233.2 (s), 233.5 (s); MS (m/z) = 660 (M^+, 29), 576 (79), 548 (40), 492 (81), 440 (100), 409 (34), 395 (28), 365 (11), 313 (8), 52 (24); HRMS calcd. for $C_{27}H_{32}O_9Cr_2Si_2$: 660.0395; found: 660.0388. Anal. Calcd. for $C_{27}H_{32}O_9Cr_2Si_2$: C, 49.08, H, 4.88; found: C, 48.80, H, 5.10.

Tricarbonyl-[η^6-2,4-dimethoxy-benzaldehyde]-chromium(0) (*rac*-**19**). A solution of **5** (100 mg, 0.36 mmol) in 2 ml of dry THF was cooled to -78 °C and 0.24 ml (0.38 mmol) *n*-BuLi (1.6 M in hexane) were added

dropwise. After stirring at -78 °C for 30 min, a solution of 0.069 ml (0.9 mmol) of DMF in 0.5 ml of dry THF was added and stirring was continued at -78 °C for 15 min and at 0 °C for 1 h. The mixture was diluted with 50 ml of EtOAc, washed with H_2O (2x50 ml) and brine (2x50 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the red oily residue was purified by PTLC (hexane/EtOAc = 3:1) to yield 84 mg (77 %) of *rac*-**19** as red needles; mp.: 119 °C; TLC (hexane/EtOAc = 3:1); IR (ATR): 3103 (w), 2947 (w), 2871 (w), 1962 (s), 1878 (s), 1678 (m), 1540 (m), 1508 (w), 1460 (w), 1289 (w), 1248 (w), 1210 (w), 1161 (w), 1018 (w), 661 (w); ^{1}H NMR (400 MHz): δ = 3.81 (s, 3 H), 3.87 (s, 3 H), 4.98 (ψd, 1 H, J = 7.0 Hz), 5.16 (d, 1 H, J = 2.3 Hz), 6.24 (d, 1 H, J = 7 Hz), 9.95 (s, 1 H); ^{13}C NMR (100 MHz): δ = 56.1 (q), 65.1 (d), 71.8 (d), 83.2 (s), 90.1 (d), 144.2 (s), 145.4 (s), 185.2 (d), 230.9 (s); MS (m/z) = 302 (M^+, 19), 218 (37), 203 (100), 188 (11), 149 (13), 97 (20), 83 (22), 69 (42), 57 (59); HRMS calcd. for $C_{12}H_{10}O_6Cr$: 301.9882; found: 301.9886. Anal. Calcd. for $C_{12}H_{10}O_6Cr$: C, 47.69, H, 3.34; found: C, 47.73, H, 3.53.

Tricarbonyl-[η^6-1,3-dimethoxy-5-methyl-benzene]-chromium(0) (**6**). A dry 250 ml Schlenk flask equipped with a reflux condenser and a Hg-bubbler was charged with a mixture of **23**[25] (5.33 g, 35 mmol), $Cr(CO)_6$ (8.0 g, 36.5 mmol) and 150 ml of *n*-Bu_2O. The whole apparatus was evacuated and flushed with argon several times. Then 15 ml of dry THF were added with a syringe and the mixture was heated to reflux for 50 h excluding light for most of the time. The solvents were removed in vacuo and the residue was recrystallized from hexane/EtOAc = 10:1 to yield 6.42 g (64 %) of **6** as yellow crystals: mp.: 137 °C; TLC (hexane/CH_2Cl_2/EtOAc = 10:1:1; hexane/EtOAc = 5:1); IR (KBr): 3446 (w), 2974 (w), 2936 (w), 1946 (s), 1866 (s), 1538 (m), 1458 (m), 1450 (m), 1323 (m), 1208 (m), 1150 (m), 678 (w), 632 (s); ^{1}H NMR (270 MHz): δ = 2.30 (s, 3 H), 3.74 (s, 6 H), 4.77 (d, 2 H, J = 2 Hz), 5.10 (t, 1 H, J = 2 Hz); ^{13}C NMR (63 MHz): δ = 21.1 (q), 55.6 (q), 67.5 (d), 75.5 (d), 108.6 (s), 143.7 (s), 234.0 (s); MS (m/z) = 288 (M^+, 73), 246 (15), 232 (43), 218 (56), 204 (100), 189 (52), 152 (14), 116 (8), 91 (13), 52 (79). Anal. Calcd. for $C_{12}H_{12}O_5Cr$: C, 50.01, H, 4.20; found: C, 50.09, H, 4.41.

Preparation of **6** *by desilylation of* **16**. To a solution of **16** (0.024 g, 0.07 mmol) in 1 ml of dry THF were added water (1 drop) and TBAF (0.4 ml, 0.4 mmol, 1 M in THF). The mixture was stirred for 2 h, diluted with EtOAc, washed with water and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by PTLC with hexane/EtOAc = 5:1 to give 17 mg (84 %) of **6** which was identified by ^{1}H NMR.

Tricarbonyl-[η^6-1,3-dimethoxy-2,5-dimethyl-benzene]-chromium(0) (**24**). *Procedure A*: A solution of 7.78 g (27 mmol) of **6** in 80 ml of dry THF was cooled to -78 °C and 18.6 ml (29.7 mmol) of *n*-BuLi (1.6 M in hexane) were added with a syringe. The mixture was stirred for 5 min at -78 °C before 2.02 ml (32.4 mmol) of MeI were injected. After 15 min the cooling bath was removed and the stirred mixture was allowed to warm to room temperature, before it was diluted with 30 ml of hexane, washed with H_2O (2x50 ml) and brine (2x50 ml) and dried over $MgSO_4$. The solvent was removed in vacuo and the oily residue crystallized from hexane/ EtOAc = 3:1 at -30 °C to yield 7.87 g (96 %) of **24** as long yellow needles. *Procedure B*: A solution of 0.120 ml (0.7 mmol) of 2,2,6,6-tetramethylpiperidine in 1.5 ml of dry THF was cooled to -78 °C and 0.380 ml (0.60 mmol) of *n*-BuLi (1.6 M in hexane) were added slowly with a syringe. The solution was allowed to warm to -40 °C and stirred for 30 min before it was recooled to -78 °C and a solution of **9** (100 mg, 0.35 mmol) in 1.5 ml of dry THF was injected. After 30 min at -60 °C, the reaction mixture was transferred with a canula to a separately prepared solution of MeI (0.110 ml, 1.75 mmol) in 2 ml of dry THF cooled to -50 °C. Stirring was continued at -50 °C for 30 min and at 0 °C for 1 h. The mixture was then diluted with 30 ml of EtOAc, washed with 2 N HCl

(2x50 ml), sat. aqueous $NaHCO_3$ and brine (2x50 ml) and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue was purified by PTLC with hexane/EtOAc = 5:1 to yield 78 mg (74 %) of **24** as long yellow needles; mp.: 145 °C; TLC (hexane/CH_2Cl_2/EtOAc = 10:1:1, hexane/EtOAc = 5:1); IR (KBr): 3108 (w), 2985 (w), 2947 (w), 2929 (w), 1934 (s), 1858 (s), 1842 (s), 1702 (m), 1526 (m), 1456 (m), 1322 (m), 1238 (m), 1143 (s), 687 (m), 636 (w); ^{1}H NMR (270 MHz): δ = 2.08 (s, 3 H), 2.29 (s, 3 H), 3.81 (s, 6 H), 4.77 (s, 2 H); ^{13}C NMR (63 MHz): δ = 9.2 (q), 21.3 (q), 55.9 (q), 72.4 (d), 86.8 (s), 106.3 (s), 142.9 (s), 234.6 (s); MS (m/z) = 302 (M^+, 23), 246 (23), 232 (5), 218 (100), 202 (15), 188 (6), 166 (6), 52 (23). Anal. Calcd. for $C_{13}H_{14}O_5Cr$: C, 51.66, H, 4.67; found: C, 51.63, H, 4.87.

Tricarbonyl-[η^6-1,3-dimethoxy-2,5-dimethyl-4-(trimethylsilyl)-benzene]-chromium(0) (**26**). A solution of **24** (0.100 g, 0.33 mmol) in 2 ml of dry THF was cooled to -95 °C and 0.25 ml (0.4 mmol) of *n*-BuLi (1.6 M in hexane) were added dropwise. After the mixture was stirred for 2 h at the same temperature, TMSCl (0.127 ml, 1 mmol) was injected. After stirring for 30 min at -95 °C and 30 min at room temperature, the mixture was diluted with EtOAc, washed with water and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the product purified by PTLC with hexane/EtOAc = 10:1 to yield 66 mg (53 %) of pure **26** as thin yellow plates; mp.: 147 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 2956 (w), 2845 (w), 1950 (s), 1868 (s), 1528 (w), 1463 (w), 1377 (w), 1333 (w), 1292 (m), 1253 (w), 1119 (m), 845 (m), 671 (m); ^{1}H NMR (400 MHz): δ = 0.43 (s, 9 H), 2.13 (s, 3 H), 2.32 (s, 3 H), 3.67 (s, 3 H), 3.79 (s, 3 H), 4.73 (s, 1 H); ^{13}C NMR (67 MHz): δ = 2.9 (q), 10.7 (q), 22.3 (q), 55.8 (q), 62.1 (q), 77.0 (d), 90.9 (s), 112.1 (s), 234.3 (s); HRMS calcd. for $C_{16}H_{22}O_5CrSi$: 374.0642; found: 374.0656; Anal. Calcd. for $C_{16}H_{22}O_5CrSi$: C, 51.33, H, 5.92; found: C, 51.30, H, 6.11.

Tricarbonyl-[η^6-1,3-dimethoxy-2-methyl-5-(trimethylsilyl)methyl-benzene]-chromium(0) (**29**). A solution of **24** (4.99 g, 16.5 mmol) in 60 ml of dry THF and 5 ml of dry HMPA was cooled to -80 °C and 11.9 ml (19 mmol) of *n*-BuLi (1.6 M in hexane) were added. After the mixture was stirred for 10 min, MeI (4 ml, 31.5 mmol) was injected and the cooling bath removed. After warming to room temperature, the mixture was partitioned between 200 ml of hexane and H_2O (100 ml). The organic layer was washed with water (100 ml) and brine (2x100 ml) and dried over $MgSO_4$. The solvent was removed in vacuo and the yellow residue recrystallized from hexane to yield 5.64 g (91%) of pure **29**; mp.: 127 °C; TLC (hexane/EtOAc = 3:1); IR (KBr): 3115 (w), 2941 (w), 2854 (w), 1949 (s), 1875 (s), 1838 (s), 1522 (m), 1404 (m), 1320 (m), 1116 (s), 856 (s), 635 (m); ^{1}H NMR (400 MHz): δ = 0.07 (s, 9 H), 1.92 (s, 2 H), 2.08 (s, 3 H), 3.79 (s, 6 H), 4.63 (s, 2 H); The constitution of **29** was proven by NOE measurements: Irradiation at 4.63 ppm (aryl. H) resulted in 6 % enhancement at 3.79 ppm (OMe), 3 % at 1.92 ppm (benzylic H) and 1 % at 0.07 ppm (TMS); ^{13}C NMR (100 MHz): δ = -1.8 (q), 19.3 (q), 26.8 (t), 55.8 (q), 71.2 (d), 85.9 (s), 111.2 (s), 143.1 (s), 234.8 (s); MS (m/z) = 374 (11), 318 (6), 291 (29), 290 (100), 73 (25), 52 (19). Anal. Calcd. for $C_{16}H_{22}O_5CrSi$: C, 51.34, H, 5.92; found: C, 51.07, H, 5.86.

Tricarbonyl-[η^6-1,3-dimethoxy-2-methyl-5-ethyl-benzene]-chromium(0) (**30**). A solution of **24** (0.300 g, 1 mmol) in 5 ml of dry THF and 1.5 ml of dry HMPA was cooled to -40 °C and 0.688 ml (1.1 mmol) of *n*-BuLi (1.6 M in hexane) were added dropwise. After the mixture was stirred for 30 min at the same temperature a solution of MeI (0.094 ml, 1.5 mmol) in 5 ml dry THF was added. The mixture was stirred for 30 min at -40 °C and for 1 h 0 °C, diluted with EtOAc, washed with 2 N HCl, sat. aquous $NaHCO_3$ and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by PTLC with hexane/EtOAc = 5:1 to give 222 mg (70 %) of **30**; mp.: 149 °C; TLC (hexane/EtOAc = 5:1); IR (ATR): 2944 (w), 2944 (w), 1937

(m), 1849 (s), 1840 (s), 1527 (w), 1445 (w), 1404 (w), 1145 (m), 917 (w), 699 (w),676 (w); ^{1}H NMR (270 MHz): δ = 1.30 (t, 3 H, J = 7.5 Hz), 2.09 (s, 3 H), 2.54 (q, 2 H, J = 7.5 Hz), 3.81 (s, 6 H), 4.78 (s, 2 H); ^{13}C NMR (67 MHz): δ = 9.3 (q), 15.1 (q), 28.6 (t), 55.8 (q), 71.1 (d), 87.1 (s), 112.6 (s), 143.0 (s), 234.5 (s); MS (m/z) = 316 (M^+, 16), 260 (11), 246 (68), 232 (100), 215 (14), 202 (7), 180 (5), 52 (43). Anal. Calcd for $C_{14}H_{16}O_5Cr$: C, 53.17, H, 5.10; found: C, 53.35, H, 5.12.

Tricarbonyl-[η^6-1,3-dimethoxy-5-n-pentyl-2-(trimethylsilyl)-benzene]-chromium(0) (**31**). A solution of **16** (0.300 g, 0.83 mmol) in 5 ml of dry THF was cooled to 0 °C and 0.575 ml (0.92 mmol) of *n*-BuLi (1.6 M in hexane) were added. After the mixture was stirred for 30 min a solution of *n*-BuI (4 ml, 31.5 mmol) in 5 ml dry THF was added dropwise. The mixture was stirred for 30 min at 0°C and for 1 h at room temperature, diluted with EtOAc, washed with 2 N HCl, sat. aquous $NaHCO_3$ and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the sensitive crude product was purified by PTLC with hexane/EtOAc = 10:1 and recrystallization from hexane. Complex **31** was obtained in 54 mg (16 %) yield as thin yellow plates. As a by-product 52 mg (30 %) of compound **33** were isolated and identified by ^{1}H NMR. **31**: mp.: 110 °C; TLC (hexane/EtOAc = 10:1); IR (ATR): 3111 (w), 2971 (w), 2954 (w), 2934 (w), 2871 (w), 1942 (s), 1874 (s), 1850 (s), 1304 (w) 1227 (m), 1114 (w), 842 (w); ^{1}H NMR (400 MHz): δ = 0.33 (s, 9 H), 0.93 (t, 3 H, J = 7 Hz), 1.39 (m, 4 H), 1.65 (m, 2 H), 2.52 (t, 3 H, J = 8 Hz), 3.69 (s, 6 H), 4.63 (s, 2 H); ^{13}C NMR (67 MHz): δ = 1.5 (q), 14.0 (q), 22.4 (t), 31.5 (t), 36.0 (t), 55.3 (q), 71.9 (d), 76.9 (s), 113.2 (s), 148.3 (s), 234.5 (s); MS (m/z) = 416 (11), 333 (32), 332 (100), 330 (19), 205 (22), 152 (9), 57 (26); HRMS calcd. for $C_{19}H_{28}O_5CrSi$: 416.1111; found: 416.1127. Anal. for $C_{19}H_{28}O_5CrSi$ calcd.: C, 54.79, H, 6.78; found: C, 55.07, H, 6.88.

1,3-Dimethoxy-5-pentyl-2-(trimethylsilyl)-benzene (**32**). A solution of **16** (0.292 g, 0.81 mmol) in 40 ml of dry THF and 1.5 ml of dry HMPA was cooled to -40 °C and 0.557 ml (0.89 mmol) of *n*-BuLi (1.6 M in hexane) were added dropwise. After the mixture was stirred for 30 min at the same temperature a solution of *n*-BuI (0.171 ml, 1.5 mmol) in 5 ml dry THF was added. The mixture was stirred for 30 min at 0°C and for 1 h at room temperature, diluted with EtOAc, washed with 2 N HCl, sat. aquous $NaHCO_3$ and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by PTLC with hexane/EtOAc = 5:1 to give a mixture of **31** and **32** in a ratio of 1 : 2. The mixture dissolved in diethylether and exposed to air and sunlight to give 129 mg (57 %) of pure **32**. TLC (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz): δ = 0.28 (s, 9 H), 0.93 (t, 3 H, J = 7 Hz), 1.38 (m, 4 H), 1.62 (m, 2 H), 2.58 (t, 3 H, J = 8 Hz), 3.72 (s, 6 H), 6.34 (s, 2 H); ^{13}C NMR (67 MHz): δ = 1.5 (q), 14.1 (q), 22.4 (t), 31.1 (t), 31.7 (t), 36.6 (t), 55.1 (q), 103.7 (d), 111.0 (s), 146.9 (s), 165.3 (s); HRMS calcd. for $C_{16}H_{28}O_2Si$: 280.1859; found: 280.1866.

1,3-Dimethoxy-5-pentyl-benzene (**33**). To a solution of **32** (0.095 g, 0.34 mmol) in 10 ml of acetic acid was added a small amount of *p*-TsOH. After stirring for 15 min the mixture was diluted with EtOAc, washed with sat. aquous $NaHCO_3$ and brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by PTLC with hexane/EtOAc = 10:1 to give 58 mg (82 %) of **33**. TLC (hexane/EtOAc = 10:1); IR (ATR): 2998 (w), 2955 (m), 2931 (m), 2871 (m), 2857 (w), 2837 (w), 1606 (s), 1595 (s), 1462 (s), 1428 (m), 1205 (s), 1149 (s), 1060 (m), 828 (w), 694 (w); ^{1}H NMR (400 MHz): δ = 0.89 (t, 3 H, J = 7 Hz), 1.32 (m, 4 H), 1.61 (m, 2 H), 2.54 (t, 2 H, J = 8 Hz), 3.72 (s, 6 H), 6.30 (t, 1 H, J = 2 Hz), 6.35 (d, 2 H, J = 2 Hz); ^{13}C NMR (100 MHz): δ = 14.0 (q), 22.5 (t), 31.0 (t), 31.5 (t), 36.3 (t), 55.2 (q), 97.5 (d), 106.5 (d), 145.4 (s), 160.6 (s); MS (m/z) = 208 (31), 166 (15), 152 (100), 151 (36), 121 (8), 91 (6); HRMS calcd. for $C_{16}H_{28}O_2Si$: 208.1463; found: 208.1477; Anal. for $C_{13}H_{20}O_2$ calcd.: C, 74.96, H, 9.68; found: C, 74.98, H, 9.71.

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