Potassium Hydride as Nucleophile: A Practical Method for Cleavage and Functional Modification of $Cr(CO)_3$−Ar−$SiMe_3$ Bonds†

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Potassium hydride reacts with $Cr(CO)_3$−aryltrimethylsilanes at room temperature to generate stabilized aryl anions which can further react with electrophiles.

Introduction

In arene−tricarbonylchromium chemistry,[1] an *o*-trimethylsilyl group has often been used as a means to effect high diastereoselectivity at benzylic centers.[1c,2] If one begins with a homochiral substrate, high diastereoselectivity implies enantioselectivity as well, and desilylation can afford an optically pure benzyl derivative in a subsequent step.[3] It is also possible to use $SiMe_3$ as a site-protecting group on the aromatic ring so that a functionalization is directed to alternative sites.[4] Cleavage of the Ar−Si bond at an appropriate stage by protiolysis or conversion of a $SiMe_3$ group to a useful functionality has a direct impact on the efficiency of a synthetic plan, an aspect that has been addressed in the present report.

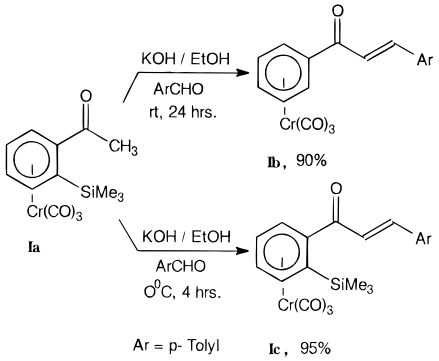
Results and Discussion

The study originated from the following two observations[5] of facile cleavage of the Ar−$SiMe_3$ bond, while attempting standard organic transformations such as aldol-dehydration (Scheme 1) and anion-assisted Cope rearrangement (Scheme 2). In both instances, desilylation could be suppressed only at low temperatures.

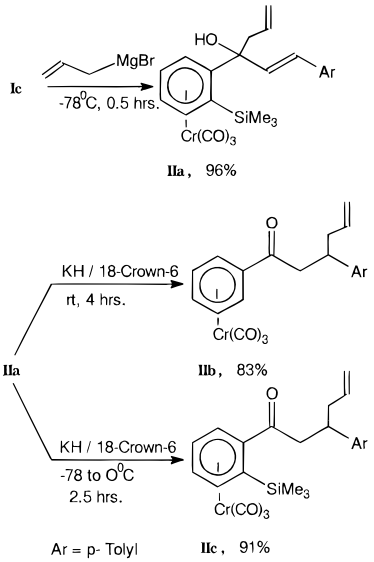
While the facility of Ar−Si bond cleavage can be attributed to stabilization of an anionic aryl group complexed with tricarbonylchromium, this observation sounds a note of caution for the use of nucleophilic bases in reactions with such substrates. We found that several common bases used in organic reactions readily effected desilylation of a chromium-complexed aromatic ring (Scheme 3). However, desilylation does not readily occur for uncomplexed arylsilanes except with fluoride ion catalysis,[6] or when strong electron-withdrawing substituents are present on the aromatic ring.[7]

We observed that potassium hydride in the presence of a catalytic quantity of 18-crown-6 (reagent A) effected

Scheme 1



Scheme 2



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† NCL Communication No. 6426.

(1) Reviews on arene tricarbonylchromium complexes: (a) Semmelhack. M. F. Transition Metal Arene Complexes: Nucleophilic Addition. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 979. (b) Semmelhack. M. F. Transition Metal Arene Complexes: Ring Lithiation. *Ibid*. p 1017. (c) Davies, S. G.; McCarthy, T. D. Transition Metal Arene Complexes: Side Chain Activation and Control of Stereochemistry. *Ibid*. p 1039.

(2) Uemura, M. Tricarbonyl (η^6-arene) chromium Complexes in Organic Synthesis. In *Advances In Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 2, pp 231−240 and refs 84−110 cited therein.

(3) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 393.

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(5) Sur, S.; Mandal, S. K.; Sarkar, A. Unpublished result.

(6) For fluoride-induced desilylation from uncomplexed aromatic ring: (a) Hayes, M. A. One or More =CH Bond(s) Formed by Substitution or Addition. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 1, pp 447−448 and refs cited therein. (b) Snieckus, V. *Chem. Rev.* **1990**, *90*, 922.

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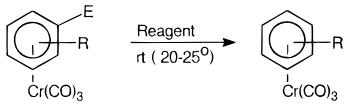
Scheme 3



1a-i **1a'-g'**

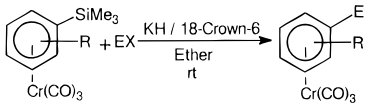
Table 1.

Substrate	R	Reagent [a]	Time(hr)	Product	Yield(%)
1a	H	A	1.25	**1a′**	77
E = $SiMe_3$		B	4.00		89
		C	5.50		70
		D	60.00		66
		E	48.00		72
1b	2-$COCH_3$	A	2.00	**1b′**	98
E = $SiMe_3$		B	2.25		92
		C	2.50		91
		D	24.00		89
		E	32.00		84
1c		A	2.00	**1c′**	91
E = $SiMe_3$		B	6.00		76
1d	2-OMe	A	1.25	**1d′**	87
E = $SiMe_3$		B	4.00		92.5
1e	4- OMe	A	1.50	**1d′**	78
E = $SiMe_3$		B	4.50		81
1f	4- Me	A	1.00	**1e′**	78
E = $SiMe_3$		B	3.50		75
1g	2,6- $(OMe)_2$	A	0.75	**1f′**	92
E = $SiMe_3$		B	3.50		92
1h	4-O-(4-$C_6H_4SiMe_3$)	A	3.00	**1g′**	91
E = $SiMe_3$		B	5.00		89
1i	H	A	1.00	**1a′**	91
E = $SnMe_3$		B	2.50		86
		D	9.00		88

[a] A = KH/18-crown-6/ether; B = 50% aq NaOH/TBAB/CH_2Cl_2; C = K_2CO_3/18-crown-6/acetone; D = KOH/EtOH; E = NaOMe/ether.

desilylation in ether in a short period of time. In a typical run, a suspension of potassium hydride in ether was added dropwise to a stirred solution of the arene−chromium complex and 18-crown-6 (10 mol %) in ether. Complete conversion of the substrate was observed (TLC) in all cases. The reaction course remained virtually unchanged when an ether solution of the complex was added to a suspension of potassium hydride in ether containing 10 mol % 18-crown-6. Sodium hydride can replace potassium hydride. Potassium or sodium hydride is believed to act as a nucleophile[8] which reacts with the tetrasubstituted silicon to initiate desilylation. In complex **1h**, $SiMe_3$ on the uncomplexed ring survives during desilylation of the complexed ring. Under biphasic conditions (reagent B), desilylation was found to reach completion within 3 to 6 h. Other mild bases such as K_2CO_3, KOH, and NaOMe can also be used for desilylation (Table 1; compounds **1a**,**b**). Tertiary amines such as triethylamine, DBU, or DABCO were not effective. Destannylation was also observed when an $SnMe_3$ group was present on the complexed aromatic ring instead of $SiMe_3$ group (Table 1; complex **1i**).

Scheme 4



1a, 1d-g **2a-k**

Table 2.

sub-strate	R	EX	time (h)	product	E	yield (%)[a]
1a	H	DMF[b]	1.0	**2a**	CHO	70 (15)
1d	2-OMe	DMF[b]	1.5	**2b**	CHO	70 (10)
1e	4-OMe	DMF[b]	1.5	**2c**	CHO	84 (6)
1f	4-Me	DMF[b]	1.0	**2d**	CHO	90 (<5)
1a	H	$(MeO)_2CO$	8.0	**2e**	CO_2Me	81 (13)
1a	H	$(EtO)_2CO$	10.0	**2f**	CO_2Et	73 (9)
1a	H	$(PhO)_2CO$	7.0	**2g**	CO_2Ph	75 (10)
1a	H	ethylene carbonate	10.0	**2h**	$CO_2(CH_2)_2OH$	78 (10)
1a	H	Ph_2CO	12.0	**2i**	$C(OH)Ph_2$	85 (<5)
1a	H	$PhCOCF_3$	4.0	**2j**	$C(OH)PhCF_3$	80 (10)
1g	2,6-$(OMe)_2$	DMF[b]	2.5	**2k**	CHO	74 (15)

[a] Numbers in parentheses indicate percentage yields of protiodesilylated products. *b* DMF was used as solvent.

The aryl anion stabilized by coordination with a $Cr(CO)_3$ group was expected to be trapped regiospecifically by electrophiles. In absence of any other electrophile, solvent DMF itself reacts with the aryl anion to afford the corresponding aromatic aldehyde complex in good yield (67−90%), along with some protiodesilylated product (5−20%), as presented in the Scheme 4 and Table 2.

Direct complexation of aromatic aldehydes with $Cr(CO)_6$ using conventional thermal method[9] is difficult due to thermal instability of the organic ligands and electron-withdrawing nature of formyl group.[10] The present method of formylation is, therefore, a clearly acceptable solution to this problem. Tricarbonylchromium complexes of a wide range of substituted aromatic aldehydes can now be conveniently prepared.[4a,11]

This method was readily adapted for introduction of other electron-withdrawing functional groups to the aromatic nucleus. When tricarbonylchromium complex of phenyltrimethylsilane (**1a**) was allowed to react with electrophiles such as ketone or dialkyl or diaryl carbonate in the presence of KH/18-crown-6 in ether, carbinol and ester complexes were obtained in moderate to good yield (see Table 2). However, protiodesilylation could not be completely suppressed. Although this reaction proceeded

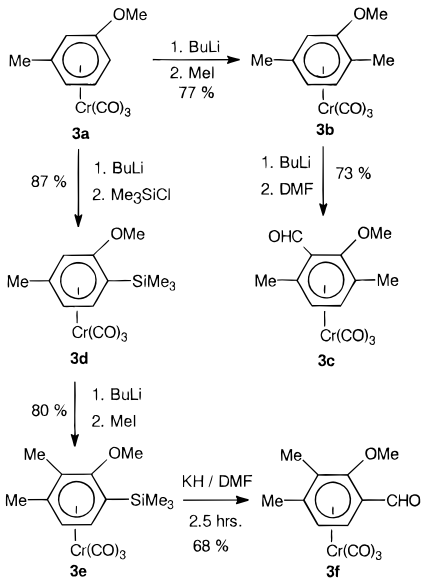
(7) For desilylation of electron defficient aromatic ring using potassium *tert*-butoxide: (a) Effenberger, F.; Spiegler, W. *Chem. Ber.* **1985**, *118*, 3900. (b) Effenberger, F.; Schollkopf, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 226. (c) Streitweiser, A.; Boerth, D. W. *J. Am. Chem. Soc.* **1978**, *100*, 755.

(8) Potassium hydride as nucleophile: Pinnick, H. W. *Org. Prepn. Proc. Int.* **1983**, *15(3)*, 199.

(9) (a) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154. (b) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381.

(10) (a) Davies, R.; Kane-Maguire, L. A. P. Chromium Compounds with η^2-η^8 Carbon Ligands. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 1001 and refs 214, 216 cited therein.

Scheme 5



much faster when DMF was used as solvent,[12] formylation (20−50%) was always a competing reaction in DMF.

Direct thermal complexation of a substrate containing more than one aromatic ring with $Cr(CO)_6$ always gives a mixture of products.[13] For instance, attempted monocomplexation of phenyl benzoate by thermolysis with $Cr(CO)_6$ yielded about 1:1 mixture of isomeric complexes.[14] In contrast, using the present method, pure complex **2g** could be readily obtained. Similarly, by proper choice of substrate and electrophile, it is possible to prepare a compound in which only the desired aromatic ring is complexed to tricarbonylchromium (see Table 2, complex: **2i**,**2j**).

One important aspect of this method of functionalization is its complete regioselectivity. Scheme 5 summarizes two routes to regioisomeric aromatic products. Normal *ortho*-lithiation of complex **3a** occurred at the sterically less congested site, and addition of methyl iodide led to the corresponding methyl substituted derivative **3b**. Subsequent treatment with BuLi generated aryl anion at the alternative site (adjacent to OMe group), where formylation could be readily effected to produce aldehyde **3c**. To obtain a regioisomer of this aldehyde, the first *ortho*-lithiated derivative from **3a** was treated with Me_3SiCl so that a silylated product **3d** was obtained. A second lithiation−alkylation led to the derivative **3e**. Now, the trimethylsilyl group was transformed to a formyl group by the procedure described in this paper, so that the complex **3f**, isomer of complex **3c**, was obtained. This sequence uses the trimethylsilyl unit as a site-protective group as well as a precursor of formyl function.

Summary

In summary, we have disclosed a facile cleavage of an $Ar-SiMe_3$ bond where the aromatic ring is complexed with tricarbonylchromium, by nucleophilic bases. Potassium or sodium hydride effects a clean reaction in aprotic medium. It is possible to trap the intermediate anionic species by different electrophiles to prepare metal-complexed arenes with electron-withdrawing functional groups. This should prove to be a useful synthetic method for such complexes since these are not readily obtainable by direct complexation route. The mild condition should tolerate a wide range of sensitive functionality as well. Further exploration of the scope and synthetic potential of this transformation is currently under way in our laboratory.

Experimental Section

All reactions were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. DMF was purified by distillation over calcium hydride under reduced pressure. Diethyl ether, dibutyl ether, and THF were freshly distilled over sodium benzophenone ketyl. Chromium hexacarbonyl and 18-crown-6 were purchased from Aldrich and used as received. Potassium hydride and sodium hydride were also purchased from Aldrich and washed with portions of hexane and anhydrous diethyl ether prior to use. Chlorotrimethylsilane was distilled over zinc powder under argon prior to use. Dimethyl and diethyl carbonate were distilled under reduced pressure. n-BuLi in hexane (ca. 1.5 M) was prepared using standard procedure and titrated prior to use. For descriptions of analytical instruments, spectral data formats and standard calibrations see ref 16. Analytical data of liquid samples (**2h**, **3c**, and 4-(trimethylsilyl)phenyl ether) were unsatisfactory.

General Procedure for Preparation of Tricarbonyl-(η^6-arene)−chromium(0) Complexes. Parent arenes of all five complexes[15a,b] (**1a**, **1d**−**f**, and **1i**) were prepared from corresponding bromo compounds via Grignard reaction followed by quenching with chlorotrimethylsilane (in case of **1a**, **1d**, **1e**, **1f**) or chlorotrimethyltin (in case of **1i**). The arene and chromium hexacarbonyl were thermolyzed in a mixture of dibutyl ether−THF (10:1) (bath temperature: 150 °C) for 12−24 h to prepare the complexes, as described in standard procedure.[9] The complexes **1b** and **1c** were prepared following reported procedures.[3]

Preparation of Tricarbonyl[η^6-2-(trimethylsilyl)resorcinol dimethyl ether]chromium(0) (1g). n-BuLi (1.56 M, 1.3 mL, 2.0 mmol) was added dropwise to a cooled (−78 °C) THF solution of tricarbonyl[η^6-resorcinol dimethyl ether]-chromium(0)[15c] (548 mg, 2.0 mmol), and the mixture was stirred at −78 °C for 2 h. Chlorotrimethylsilane (218 mg, 0.3 mL, 2 mmol) was added, and stirring was continued (−78 °C, 2 h). Degassed methanol (5 mL) was slowly added to quench the reaction, and the mixture was allowed to reach room temperature. Solvent was evaporated to afford the crude complex, which was purified by column chromatography. Recrystallization from dichloromethane−hexane gave the title compound as yellow crystals (554 mg, 80%), mp 145 °C; ^{1}H NMR ($CDCl_3$): 0.35 (s, 9H), 3.70 (s, 6H), 4.72 (d, 2H, J = 6.5 Hz), 5.73 (t, 1H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$): 1.8, 55.6, 70.0,

(11) Synthetic uses of some substituted aromatic aldehyde complexes: (a) Sur, S.; Mandal, S. K.; Sarkar, A. Unpublished results. (b) Reference 1c pp 1044−1048 and refs cited therein. (c) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem*. **1996**, *61*, 6088. (d) Mukai, C.; Hirai, S.; Kim, I. J.; Hanaoka, M. *Tetrahedron Lett*. **1996**, *37*, 5389.

(12) When DMF was used as the solvent, reaction was complete within 2 h. In ether it took more than 5 h for completion.

(13) Reference 10, p 1010.

(14) Thermal complexation of phenyl benzoate resulted in a mixture of three products (15:10:1). In first major product $Cr(CO)_3$ anchored on the electron rich phenoxy ring and the second major product is the same as **2g**, and in the minor product both rings complexed to $Cr(CO)_3$.

(15) (a) Seyferth, D.; Alleston, D. L. *Inorg. Chem*. **1963**, *2*, 417. (b) Effenberger, F.; Schollkopf, K. *Chem. Ber*. **1985**, *118*, 4356. (c) Mcfarlane, W.; Grim, S. O. *J. Organomet. Chem*. **1966**, *5*, 147. (d) Nicholls, B.; Whiting, M. C. *J. Chem. Soc*. **1959**, 551. (e) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 192. (f) Mahaffy, C. A. L.; Hamilton, J. *Synth. React. Inorg. Met. Org. Chem*. **1987**, *17*, 43. (g) Mahaffy, C. A. L. *Ibid*. **1984**, *14*, 679.

(16) Chowdhury, S. K.; Samanta, U.; Puranik, V. G.; Sarkar, A. *Organometallics* **1997**, *16*, 2618.

81.1, 93.6, 148.7, 234.5; IR ($CHCl_3$): 1960, 1860 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_5SiCr$: C: 48.55, H: 5.24. Found: C: 48.51, H: 5.32.

Preparation of Tricarbonyl[η^6-4-(trimethylsilyl)phenyl ether]chromium(0) (1h). Grignard reaction of 4-bromophenyl ether (10 g, 0.03 mol) and magnesium (0.063 mol) in ether followed by quenching with trimethylsilyl chloride (7 g, 0.065 mol) gave 4-(trimethylsilyl)phenyl ether as colorless oil (7 g, 73%), bp 150 °C (Kugelrohr bath temp)/1.0 mm; ^{1}H NMR ($CDCl_3$): 0.45 (s, 18H), 7.17 (d, 4H, J = 8.6 Hz), 7.66 (d, 4H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$): −0.68, 129.90, 134.60, 135.10, 158.13; IR ($CHCl_3$): 3020, 1580, 1480 cm^{-1}; mass: M^+ = 314. 4-(Trimethylsilyl)phenyl ether was (3 g, 9.55 mmol) subjected to complexation under standard condition using chromium hexacarbonyl (3 g, 13.6 mmol), dibutyl ether (100 mL), and THF (10 mL) to yield the title compound **1h** as yellow crystals (1.85 g, 43%), mp 93−95 °C; ^{1}H NMR ($CDCl_3$): 0.29 (s, 9H), 0.31 (s, 9H), 5.10 (d, 2H, J = 6.4 Hz), 5.54 (d, 2H, J = 6.4 Hz), 7.19 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): −0.83, −0.32, 80.0, 94.14, 99.70, 120.85, 135.56, 138.47, 143.77, 153.90, 233.60; IR ($CHCl_3$): 1960, 1880 (br), 1590, cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_4Si_2Cr$: C: 55.98, H: 5.82. Found: C: 56.06, H: 5.90.

General Procedure for Desilylation. Using reagent A (KH/18-crown-6/ether): To a solution of the complex (*n* mmol) and 18-crown-6 (10 mol %) in ether (5*n* mL) was added dropwise a suspension of KH (1.2−1.3*n* mmol) in ether (3*n* mL) with stirring at room temperature. After complete consumption of starting material (TLC), the reaction was quenched with degassed water at 0−5 °C, and the product was extracted with ether.

Using reagent B (50% aq NaOH/TBAB/CH_2Cl_2): To a solution of the complex (*n* mmol) and tetrabutylammonium bromide (TBAB, 10 mol %) in CH_2Cl_2 (3*n* mL) was added 50% aq NaOH (*n* mL) dropwise with stirring at room temperature. After completion of reaction (TLC), it was diluted with water and extracted with dichloromethane.

Using reagent C (K_2CO_3/18-crown-6/acetone): A solution of the complex (*n* mmol) in acetone (5*n* mL) was added dropwise to a stirred suspension of K_2CO_3 (1.5*n* mmol) and 18-crown-6 (10 mol %) in acetone (3*n* mL) at room temperature. After completion of the reaction (TLC), inorganic salts were removed by filtration. Crude complex obtained after evaporation of acetone was purified by chromatography.

Using reagent D (KOH/EtOH): To a solution of the complex (*n* mmol) in EtOH (5*n* mL) was added 1.5*n* mmol KOH in ethanol (1 mL) dropwise with stirring at room temperature. After completion of reaction (TLC), the reaction mixture was diluted with water and the product was extracted with dichloromethane.

Using reagent E (NaOMe /ether): A solution of the complex (*n* mmol) in ether (5*n* mL) was added dropwise to the stirred suspension of NaOMe (1.5*n* mmol) in ether (3*n* mL) at room temperature. After completion of reaction it was quenched with degassed water under ice-cold conditions and extracted with ether.

Several of the desilylated products have been reported earlier: **complex 1a′**: ref 15d, **complex 1b′**: ref 15d, **complex 1c′**: ref 3, **complex 1d′**: ref 15d, **complex 1e′**: ref 15d, **complex 1f′**: ref 15c.

Complex 1g′: yellow crystalline solid; mp 140 °C; ^{1}H NMR ($CDCl_3$): 0.3 (s, 9H), 4.89 (t, 1H, J = 6.3 Hz); 5.15 (d, 2H, J = 6.3 Hz), 5.55 (t, 2H, J = 6.3 Hz), 7.17 (d, 2H, J = 8.5 Hz), 7.51 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$): −1.20, 76.93, 85.62, 94.26, 120.31, 135.20, 136.13, 142.04, 153.48, 232.85; IR ($CHCl_3$): 1985, 1915 (br) cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_4SiCr$: C: 57.13, H: 4.79. Found: C: 57.10, H: 4.85.

General Procedure for the Functionalization of Cr(CO)$_3$-Complexed Arylsilanes. To a solution of the complexed arylsilane (*n* mmol), electrophile (EX), (1.5*n* mmol), and 18-crown-6 (10 mol %) in ether (5*n* mL) was added a suspension of KH (1.2−1.3n mmol) in ether (3*n* mL) dropwise with stirring at room temperature. When the electrophile was DMF, it was used as the solvent also. After completion of the reaction, the reaction mixture was quenched with degassed water at ice cold temperature and extracted with ether. Crude complex obtained after evaporation of solvent was purified by chromatography. Some products have been reported earlier. viz, **complex 2a**: ref 15b, **complex 2b**: ref 15e, **complex 2e**: ref 15d, **complex 2f**: ref 15f, **complex 2i**: ref 15b.

Complex 2c: eed crystalline solid; mp 108−110 °C; ^{1}H NMR ($CDCl_3$): 3.80 (s, 3H), 5.22 (d, 2H, J = 6.7 Hz); 6.08 (d, 2H, J = 6.7 Hz), 9.40 (s, 1H); ^{13}C NMR ($CDCl_3$): 55.9, 76.8, 90.6, 94.6, 144.8, 186.6, 230.0; IR ($CHCl_3$): 1985, 1915 (br), 1690 cm^{-1}. Anal. Calcd for $C_{11}H_8O_5Cr$: C: 48.54, H: 2.96. Found: C: 48.63, H: 2.97.

Complex 2d: red crystalline solid; mp 90 °C; ^{1}H NMR ($CDCl_3$): 2.35 (s, 3H), 5.17 (d, 2H, J = 6.4 Hz); 6.00 (d, 2H, J = 6.4 Hz), 9.46 (s, 1H); ^{13}C NMR ($CDCl_3$): 20.6, 90.4, 93.0, 95.1, 112.1, 187.3, 230.2; IR ($CHCl_3$): 1985, 1915 (br), 1690 cm^{-1}. Anal. Calcd for $C_{11}H_8O_4Cr$: C: 51.56, H: 3.15. Found: C: 51.49, H: 3.14.

Complex 2g: orange crystalline solid; mp 100 °C; ^{1}H NMR ($CDCl_3$): 5.35 (t, 2H, J = 6.6 Hz); 5.65 (t, 1H, J = 6.6 Hz), 6.27 (d, 2H, J = 6.6 Hz), 7.21 (d, 2H, J = 8.4 Hz), 7.29 (t, 1H, J = 8.4 Hz), 7.45 (t, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): 88.4, 89.9, 95.0, 121.7, 126.5, 129.8, 150.6, 164.5, 230.8; IR ($CHCl_3$): 1980, 1910 (br), 1730 cm^{-1}. Anal. Calcd for $C_{16}H_{10}O_5Cr$: C: 57.49, H: 3.03. Found: C: 57.51, H: 3.13.

Complex 2h: red oil; ^{1}H NMR ($CDCl_3$): 2.09 (brs, 1H), 3.94 (m, 2H), 4.48 (m, 2H), 5.32 (t, 2H, J = 6.4 Hz), 5.58 (t, 1H, J = 6.4 Hz), 6.15 (d, 2H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$): 60.9, 67.3, 89.2, 89.6, 94.6, 94.7, 165.9, 230.8; IR ($CHCl_3$): 3600−3300 (br), 1980, 1910 (br), 1720 cm^{-1}.

Complex 2j: yellow crystals; mp 130 °C; ^{1}H NMR ($CDCl_3$): 2.98 (s, 1H), 5.00 (t, 1H, J = 6.7 Hz); 5.18 (m, 2H), 5.55 (t, 1H, J = 6.7 Hz), 6.16 (d, 1H, J = 6.7 Hz), 7.45 (m, 3H), 7.65 (m, 2H); ^{13}C NMR ($CDCl_3$): 87.3, 88.2, 94.9, 96.0, 96.1, 109.4, 127.1, 128.7, 129.7, 137.0, 231.8; IR ($CHCl_3$): 1975, 1895 (br) cm^{-1}. Anal. Calcd for $C_{17}H_{11}O_4F_3Cr$: C: 52.59, H: 2.86. Found: C: 52.68, H: 2.93.

Complex 2k: red crystalline solid; mp 130 °C dec; ^{1}H NMR ($CDCl_3$): 3.81 (s, 6H), 4.82 (d, 2H, J = 6.3 Hz), 5.82 (t, 1H, J = 6.3 Hz), 10.1 (s, 1H); ^{13}C NMR ($CDCl_3$): 56.3, 68.7, 91.9, 103.9, 145.1, 185.2, 231.2; IR ($CHCl_3$): 1975, 1895 (br), 1680 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_6Cr$: C: 47.68, H: 3.34. Found: C: 47.58, H: 3.36.

Preparation of Tricarbonyl[η^6-3-methylanisole]chromium(0) (3a). 3-Methylanisole (3 g, 25 mmol) was subjected to complexation under standard condition using chromium hexacarbonyl (3 g, 13.6 mmol), dibutyl ether (100 mL), and THF (10 mL) to yield the title compound **3a** as yellow crystals (2.2 g, 63%), mp 80 °C; ^{1}H NMR ($CDCl_3$): 2.25 (s, 3H), 3.69 (s, 3H), 4.75 (d, 1H, J = 6.0 Hz), 5.03 (d, 1H, J = 6.0 Hz), 5.08 (s, 1H), 5.56 (t, 1H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$): 20.96, 55.63, 76.30, 80.76, 87.12, 95.40, 111.23, 144.00, 233.90; IR ($CHCl_3$): 1960, 1880 (br), cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_4Cr$: C: 51.17, H: 3.90. Found: C: 51.32, H: 4.02.

Preparation of Tricarbonyl[η^6-2,5-dimethylanisole]chromium(0) (3b).[15g] Following the same procedure as used for **1g**, it was prepared from **3a** (516 mg, 2.0 m mol), using n-BuLi (1.56 M, 1.3 mL, 2.0 mmol) and methyl iodide (300 mg, 0.15 mL, 2.1 mmol). Recrystallization from dichloromethane−hexane gave the title compound as yellow crystals (419 mg, 77%).

Preparation of Tricarbonyl[η^6-2-methoxy-3,6-dimethylbenzaldehyde]chromium(0) (3c). As described above it was prepared from **3b** (272 mg, 1.0 mmol) using n-BuLi (1.56 M, 0.7 mL, 1.0 mmol) and DMF (109 mg, 0.1 mL, 1.5 mmol). Recrystallization from dichloromethane−hexane gave the title compound as a red viscous oil (219 mg, 73%); ^{1}H NMR ($CDCl_3$): 2.20 (s, 3H), 2.45 (s, 3H), 3.79 (s, 3H), 4.79 (d, 1H, J = 6.3 Hz), 5.74 (d, 1H, J = 6.3 Hz), 10.06 (s, 1H); ^{13}C NMR ($CDCl_3$): 22.96, 30.00, 31.80, 64.30, 84.45, 89.07, 91.1, 131.48, 146.67, 188.90, 230.74; IR ($CHCl_3$): 1975, 1900 (br), 1680 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_5Cr$: C: 52.00, H: 4.03. Found: C: 52.03, H: 4.06.

Preparation of Tricarbonyl[η^6-2-(trimethylsilyl)-5-methylanisole]chromium(0) (3d). It was prepared from **3a** (258 mg, 1.0 m mol) following the same procedure as above

using n-BuLi (1.56 M, 0.7 mL, 1.0 m mol) and trimethylsilyl chloride (110 mg, 0.15 mL, 1.0 mmol). Recrystallization from dichloromethane−hexane gave the title compound as yellow crystals (287 mg, 87%), mp 125 °C; ^{1}H NMR ($CDCl_3$): 0.28 (s, 9H), 2.28 (s, 3H), 3.73 (s, 3H), 4.68 (d, 1H, J = 6.4 Hz), 4.89 (s, 1H), 5.33 (d, 1H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$): −0.45, 21.20, 55.40, 76.60, 87.21, 87.42, 101.70, 111.51, 147.96, 234.25; IR ($CHCl_3$): 1955, 1895, 1870, cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_4SiCr$: C: 50.90, H: 5.49. Found: C: 50.88, H: 5.48.

Preparation of Tricarbonyl[η^6-2,3-dimethyl-6-(trimethylsilyl)anisole]chromium(0) (3e). It was prepared from **3d** (330 mg, 1.0 mmol) following the same procedure as above, using n-BuLi (1.56 M, 0.7 mL, 1.0 mmol) and methyl iodide (300 mg, 0.15 mL, 2.1 mmol). Recrystallization from dichloromethane−hexane gave the title compound as yellow crystals (275 mg, 80%), mp 110 °C. ^{1}H NMR ($CDCl_3$): 0.38 (s, 9H), 2.20 (s, 3H), 2.31 (s, 3H), 3.76 (s, 3H), 4.86 (d, 1H, J = 6.7 Hz), 5.38 (d, 1H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$): 0.00, 13.33, 19.33, 62.33, 90.67, 91.67, 98.67, 101.00, 112.00, 147.67, 234.33; IR ($CHCl_3$): 1940, 1860 (br) cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4SiCr$: C: 52.31, H: 5.85. Found: C: 52.30, H: 5.91.

Preparation of Tricarbonyl[η^6-2-methoxy-3,4-dimethylbenzaldehyde]chromium(0) (3f). Following the general procedure of functionalization it was prepared from **3e** (172 mg, 0.5 mmol) using DMF (5 mL), 18-crown-6 (13 mg, 10 mol %), and KH (26 mg, 0.65 mmol). Recrystallization from dichloromethane−hexane gave the title compound as red crystals (102 mg, 68%), mp 135 °C. ^{1}H NMR ($CDCl_3$): 2.21 (s, 3H), 2.40 (s, 3H), 3.85 (s, 3H), 5.00 (d, 1H, J = 6.5 Hz), 5.99 (d, 1H, J = 6.5 Hz), 9.90 (s, 1H); ^{13}C NMR ($CDCl_3$): 12.18, 19.62, 64.72, 89.12, 89.14, 90.66, 99.90, 111.10, 144.36, 185.80, 231.00. IR ($CHCl_3$): 1945, 1870 (br), 1660 cm^{-1}. Anal. Calcd for $C_{13}H_{12}O_5Cr$: C: 52.00, H: 4.03. Found: C: 52.03, H: 4.00.

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