Multiple substitutions on (η⁶-arene)tricarbonylchromium(0) complexes

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The treatment of representative (η⁶-arene)tricarbonylchromium(0) complexes **1a–c** and **4** with 3 equivalents of LiTMP followed by an electrophilic quench with Me₃SiCl provided a series of trisilylated complexes **2a–c** and **5a**. The use of Me₃SnCl and Ph₂PCl as electrophile also yielded unusual trisubstituted complexes **13a** and **13b**. The X-ray crystallographic structure of complex **13b** is reported. Deuteration studies using deuteroacetic acid as the electrophile led to the observation of a trideuterated species presumably derived from a trianionic species formed during the reaction. Efficient disubstitution was observed when complexes **7**, **9** and **11** were treated with 3 equivalents of LDA followed by an electrophilic quench with Me₃SiCl

Introduction

Carbanions have always played an important role in synthetic organic chemistry.[1] The developments in this area have been enormous and covalent bond formation based on carbanionic intermediates is now a formidable tool in the organic chemists' arsenal. The strategy is routinely used to create complex molecular structures and to generate chiral centres in asymmetric synthesis.[2] In most cases, the approach involves the *in situ* generation of a mono-metallated species and its subsequent quench by a suitable electrophile; the introduction of more than one electrophile is usually achieved by an iterative strategy.[3]

In contrast, reports detailing the generation of di- and trianions (multiple metallated species) where the negative charge is carbon-based are rather rare and the use of such species in organic synthesis is relatively scarce.[4] Especially, there are very few reports detailing the generation and use of di- and trimetallated aromatics.[5] In particular, generation of a multiple anion on benzene and its subsequent functionalization is severely limited due to the need to use extremely harsh conditions (lithium vapour)[6] for such a transformation. The best route to date to such species involves subjecting the corresponding polyhalo-benzene to lithium–halogen exchange using alkyllithium reagents such as LiDBB (4,4′-di-*tert*-butyl-biphenylyllithium),[5,7] though slight variations in reaction temperature often led to intractable mixtures.[7a,b]

In parallel, the characteristic, enhanced kinetic acidity of (η⁶-arene)tricarbonylchromium(0) complexes has been utilised regularly for the introduction of a single substituent *via* a deprotonation–electrophilic quench sequence and has been the subject of numerous synthetic and mechanistic studies.[8] As in the case of uncomplexed aromatic substrates, reports regarding the introduction of two new substituents employing a similar sequence are relatively few.[9] Although such double functionalisation has been mentioned in the literature, and in one case has been elegantly exploited in a sophisticated synthesis,[9c] this reactivity has never been the target of a systematic study. Typically, reports mention the formation of such products as unwanted side-products of a lithiation–electrophilic quench.

Furthermore, to the best of our knowledge, there exist only two examples of trisubstitution. In the first, chlorination of tricarbonyl(η⁶-chlorobenzene)chromium(0) afforded a tetra-substituted complex as a side product in poor yield.[9f] In the second report, we observed a single trisubstitution

Table 1 Reaction of complexes **1a–c**
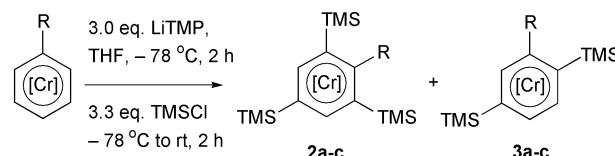
1a, R = SO₂^{t}Bu
**1b,** R = OMe
1c, R = CH₂NMe₂

[Cr] = Cr(CO)₃

Entry	R	Yield of 2 (%)	Yield of 3 (%)
1	SO₂^{t}Bu	50	[a]
2	OMe	42	9
3	CH₂NMe₂	40	48

[a] Compound **3a** was not observed.

reaction as part of a wide ranging study on the reactivity of an electron-deficient sulfone complex.[9d] We report here the results of a more detailed investigation of multiple substitution of (η⁶-arene)tricarbonylchromium(0) complexes. Some of the material described herein has been reported as a preliminary communication.[10]

Results and discussion

Recently, we reported the results of a reactivity study of a relatively uncommon, electron-deficient complex **1a**.[9d] During the course of our study we discovered that treatment of sulfone complex **1a** with three equivalents of the base, 2,2,6,6-tetramethylpiperidinyllithium (LiTMP), at −78 °C for two hours followed by an electrophilic quench with TMSCl led to the isolation of the trisilylated complex **2a** in 50% yield as the only product (Table 1, Entry 1). Due to the lack of precedent for such a transformation, we initially believed that this unusual reaction may be limited to the highly electron-poor substrate **1a**, the electron-withdrawing nature of the sulfone group being responsible for the increased stabilisation of a species bearing carbon-based negative charges. In spite of the exceptional nature of the reaction and our suspicions about its limitations,

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Table 2 Optimisation studies for the synthesis of **5a**

[Cr] = Cr(CO)$_3$
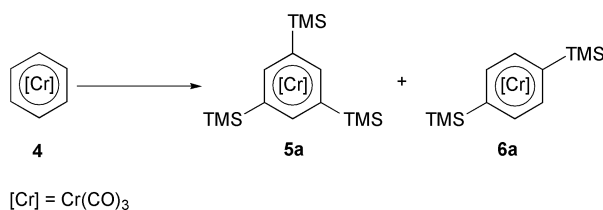
Entry	Deprotonation time/h	Base	Deprotonation Temp./°C	Ratio of **5a** : **6a**	Overall yield (%)
1	0.5	LiTMP	−78	28 : 72	78
2	2	LiTMP	−78	29 : 71 (26 : 63)[a]	89
3	6	LiTMP	−78	30 : 70	87
4	2	LiTMP	−40	38 : 62	87
5	2	LDA	−78	42 : 58	89
6	2	LDA	−40	46 : 54 (39 : 46)[a]	86
7	2	LDA	−20	[b]	18

[a] Isolated yields in parentheses (%). [b] Extensive decomposition was observed, overall yield <20%.

we speculated that this unique reactivity may be associated with the tricarbonylchromium(0) moiety and may prove to be more general. In order to test our conjecture, we attempted the reaction on the electron-rich (η^6-anisole)tricarbonylchromium(0) complex **1b**. To our delight, treatment of **1b** with LiTMP followed by TMSCl quench under identical conditions afforded the novel trisilylated complex **2b** along with a 2,5-disilylated product **3b**[9e] (Table 1, Entry 2). This result indicated that the trisubstitution was a more general reaction than we had initially believed and was indeed not entirely determined by the electron withdrawing ability of the sulfone group. The structures of complexes **2b** and **3b** were unambiguously assigned from their NOESY spectra. A positive NOE was observed between the aromatic proton signal and both the TMS signals for **2b**. The OMe signal also showed a positive NOE with the 2 identical TMS groups, confirming a 2,4,6 disposition of the TMS groups. In the case of **3b**, the aromatic proton which appeared as a singlet showed a positive NOE with the OMe and one of the TMS signals, while the doublets interacted with only the TMS signals, confirming the TMS groups were incorporated in the 2 and 5 positions of the aromatic ring. In order to further probe the scope of the reaction, we chose to perform the same reaction on the tricarbonyl(η^6-N,N-dimethylbenzylamine)-chromium(0) complex **1c**. The neutral complex **1c** was attractive as it is a common motif in a large number of natural products and success would offer the possibility of using this new methodology in the synthesis of interesting target molecules. Pleasingly, the reaction proceeded smoothly to afford the novel complex **2c** albeit accompanied by the novel disubstituted complex **3c** (Table 1, Entry 3). Having successfully performed the trisubstitution on electron-poor, neutral and electron-rich complexes, we turned our attention to the unsubstituted (η^6-benzene)tricarbonylchromium(0) complex **4**. The anticipated product would not only have a C_{3v} element of symmetry, but could also be envisaged as a precursor for a variety of molecules having interesting material properties, in particular starburst dendrimers. As detailed in the literature the multiple functionalisation of benzene is indeed a challenge. The few known methods of trisubstitution have to proceed *via* the corresponding trihalo-benzene. We were, thus, excited at the possibility of gaining access to complexes having C_3 symmetry, from the benzene unit itself. With such a goal in mind, we subjected the unsubstituted benzene complex **4** to the now established protocol of trisubstitution. Treatment of (η^6-benzene)tricarbonylchromium(0) complex **4** with 3 equivalents of LiTMP at −78 °C followed by a TMSCl quench led to the novel complex **5a** and **6a**[11] in 89% overall yield as a mixture in the ratio 29 : 71 of **5a** : **6a** (Table 2, Entry 2). The mixture

was separated by column chromatography to afford pure **5a** (26%) and **6a** (63%).

A control experiment was performed under identical conditions: uncomplexed benzene was stirred with 3 equivalents of LiTMP at −78 °C for 2 hours. Quenching the reaction mixture with TMSCl led to recovery of starting material (>95%), establishing that the unique reactivity was indeed a result of the activating effect of the tricarbonylchromium(0) unit.

Though the trisubstitution could be performed on the unsubstituted complex **4**, the synthetic utility of the reaction was somewhat marred by the isolation of a mixture of products, wherein our desired trisubstituted product was not the major component (Table 2, Entry 2). We thus proceeded to optimise the reaction conditions in order to maximise the formation of the desired trisilylated complex. Three variables were investigated, a) time allowed for deprotonation, b) base structure, and c) temperature of deprotonation. The results are summarised in Table 2 and the salient findings are described below:

a) Reactions were attempted where the time allowed for deprotonation of the complex with 3 equivalents of LiTMP was varied. Changing the deprotonation time from 0.5 h to 6.0 h did not show any significant change in the relative distribution of the products (Table 2, Entries 1–3).

b) The reaction temperature was increased from −78 to −40 °C; the amount of the desired trisilylated product increased notably on performing the deprotonation at −40 °C (Table 2, Entry 4).

c) The use of a structurally similar, yet comparatively less hindered amide base, LDA, was found to lead to a higher ratio of the tri- : disilylated complexes (Table 2, Entry 5). The use of amide bases was found to be necessary for multiple functionalisation: use of n-BuLi as a base gave no trisubstitution at all.

d) The highest yield of complex **5a** was obtained upon stirring the substrate with LDA at −40 °C for a period of 2 h (Table 2, Entry 6). Attempts to perform the reaction at temperatures higher than −40 °C resulted in extensive decomposition of the substrate and led to substantially lower yields (Table 2, Entry 7).

Based on the results of the optimisation studies we then decided to carry out further investigations at −40 °C, using LDA as the base and allowing 2 hours as the time for deprotonation.
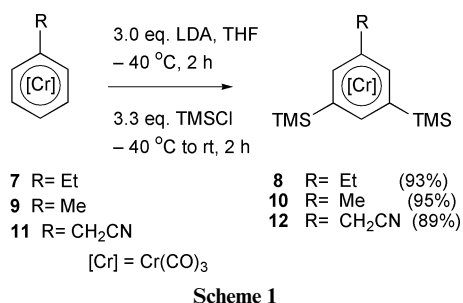
We next attempted to functionalise alkyl substrates using our now established trisubstitution protocol. Treatment of tricarbonyl(η^6-ethylbenzene)chromium(0) complex **7** with 3 equivalents of LDA at −40 °C, followed by a TMSCl quench led to the isolation of the corresponding 3,5-disilylated complex **8** in 93% yield as the only product. Tricarbonyl(η^6-

Table 3 Reaction of complex **4** with various electrophiles

[Cr] = Cr(CO)₃ — scheme showing **4** reacting with 3.0 eq. LDA, THF, −40 °C, 2 h; then 3.3 eq. ECl, −40 °C to rt, 2 h to give **13a**, E = SnMe₃; **13b**, E = PPh₂ and **14a–b**

| Entry	E	Yield of **13** (%)	Yield of **14** (%)
1	SnMe₃	58	7
2	PPh₂	29	a

a Compound **14b** was observed, but was not isolated.

toluene)chromium(0) complex **9** also afforded the 3,5-disilyl-ated complex **10** in excellent yield (95%). An analogous 3,5-disilylated complex **12** was also isolated in excellent yield (89%) on treatment of (η^6-benzylnitrile)tricarbonylchromium(0) complex **11** with 3 equivalents of LDA at −40 °C, followed by a TMSCl quench (Scheme 1).

7 R= Et **9** R= Me **11** R= CH₂CN — 3.0 eq. LDA, THF, −40 °C, 2 h; then 3.3 eq. TMSCl, −40 °C to rt, 2 h — **8** R= Et (93%), **10** R= Me (95%), **12** R= CH₂CN (89%)

[Cr] = Cr(CO)₃

Scheme 1

As we had limited ourselves to the use of silicon electrophiles until now, it was clear that the scope and utility of the reaction could be improved further by the use of different electrophiles. Considering the widespread use of tin containing compounds in organic synthesis,[12] particularly in coupling reactions, we chose Me₃SnCl as our first new electrophile. The [η^6-1,3,5-tris(trimethylstannyl)benzene]tricarbonylchromium(0) complex **13a** is envisaged as a precursor to a variety of trisubstituted target molecules. Treatment of unsubstituted (η^6-benzene)-tricarbonylchromium(0) complex **4** with 3 equivalents of LDA at −40 °C was followed by a Me₃SnCl quench. The temperature of the reaction mixture was allowed to rise to room temperature. Column chromatography led to the isolation of novel complex **13a** in good yield with **14a**[13] as the minor product (Table 3, Entry 1).

The utility of phosphine ligands in catalysis cannot be over-stated. A large variety of such compounds have been synthesised and tested as ligands for transition metal mediated catalytic reactions.[14] Consequently there is a constant demand for the design and synthesis of new phosphine containing ligands. However, there is a surprising paucity of reports highlighting the use of C_{3v} symmetric phosphine ligands,[15] the reason being the difficulty of synthesis of this class of compound. The only report detailing the synthesis of 1,3,5-tris(diphenylphosphino)benzene mentions that the desired ligand could be synthesised in low yield only and could not be adequately purified.[16] We, thus, tried to use our trisubstitution protocol to access the tricarbonylchromium(0) derivative of this interesting class of compound. The use of PPh₂Cl as the electrophile led to the formation of a mixture of complexes **13b** and **14b**. The mixture was inseparable by column chromatography but fractional crystallisation led to the isolation of the novel trisubstituted complex **13b** (Table 3, Entry 2). The complex was fully characterised and its structure confirmed by
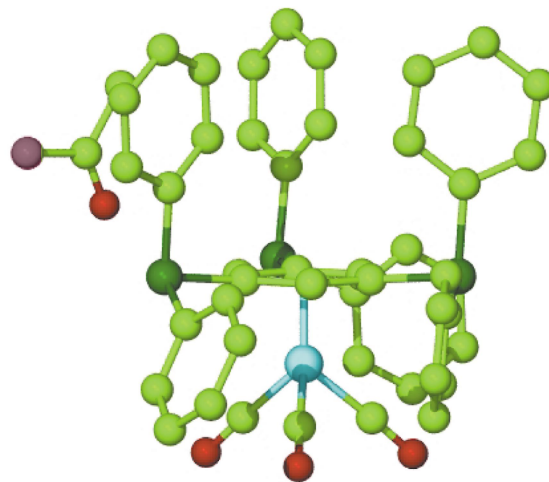
Fig. 1 X-Ray crystallographic structure of **13b**.

X-ray crystallography (Fig. 1). The molecule adopts C_1 symmetry, creating a lattice pocket for the inclusion of a molecule of acetone, held in place by C–H⋯π and C–H⋯O interactions although NMR results indicate that the solution conformation is C_3 symmetric. The phosphorus atoms are located slightly out of the plane of the η^6-arene ring away from the metal centre (deviation 0.096–0.146 Å), possibly as a consequence of unfavourable phenyl–CO steric interactions. The phenyl groups on the metal side of the η^6-arene ring are orientated to maximise C–H⋯O hydrogen bonding interactions to the oxygen of the CO ligands. Within the metal bound arene, C–C bond distances exhibit slight alternation, while Cr–C$_{arene}$ distances fall into two distinct groups, with longer distances observed to the phosphorus-bound atoms C(4), C(6) and C(8) of 2.226(16) Å average and shorter bonds to the odd-numbered carbon atoms of 2.1934(16) Å average.

To gain an insight into the species involved in the reactions described above, we decided to use deuteroacetic acid as an electrophilic quench. As the electrophile is incompatible with LDA, it should provide information about the various species formed on treatment of (η^6-arene)tricarbonylchromium(0) complexes with 3 equivalents of LDA. The reaction mixture from **1a** was therefore quenched with deuteroacetic acid and worked up as usual. The mass spectrum of the resultant yellow solid showed the presence of 4 molecular ion peaks corresponding to the presence of the unreacted **1a**, and its mono, di and trideuterated analogues in the ratio 14 : 38 : 35 : 13. The presence of a significant amount of the trideuterated complex strongly suggests the formation of a trianion. To consolidate our observation regarding the formation of a trianion, we repeated the deuteration experiment on substrate **1b**. The mass spectrum of the resultant mixture again showed the existence of a trideuterated species (25 : 45 : 24 : 6) and again suggests the formation of a trianion.

The regiochemical outcome of all the trisubstitutions detailed above may be predicted by assuming that multiple anions are generated and that the charges arrange themselves to be as far apart as possible thus achieving minimum electronic repulsion. Thus it appears that **5a** and **6a** result from the most stable tri- and dianions available to the (η^6-benzene)tricarbonyl-chromium(0) complex **4**. In the cases of **1a**—**c**, the substituent favours an *ortho* anion and **2a**—**c** and **3a**—**c** appear to be the products of the corresponding tri- and dianions of least energy. In the case of **7**, **9** and **11**, it seems that *meta* anion formation is favoured and once again, the most stable polyanionic situation is generated (the *meta* directing effect of the alkyl substituents may be attributed to their weak electron releasing nature and/or their steric bulk). Whilst the intermediacy of polyanions in the reaction is by no means certain, the above rationale provides a

simple method for predicting the outcome of multiple substitutions of (η^6-arene)tricarbonylchromium(0) complexes.

Conclusion

In summary, we have carried out a detailed investigation of an unusual one-pot trisubstitution reaction. We have broadened the scope of the reaction by successfully performing the reaction on a representative range of complexes and using several electrophiles.

This methodology complements the existing methods of generating polymetallated aromatic species which involves either lithium–halogen exchange of suitable trihalogenated aromatic substrates such as 15[7c,d] or the *ortho*-lithiation of substrates bearing strongly electrophilic substituents such as 16 (Scheme 2).[5] The new method obviates the need to synthesise

LiDBB = Lithium 4,4′-di-*tert*-butylbiphenyl   [Cr] = Cr(CO)$_3$
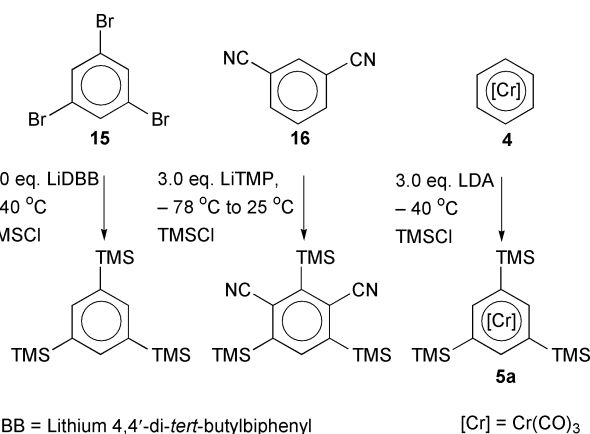
Scheme 2

appropriately substituted poly-halogenated benzenes, the synthesis of which may be challenging, especially in the presence of other substituents, or the need to use directing groups which are unlikely to be required in the target molecule.

Finally it is of interest to note that the tricarbonylchromium(0) unit may be equated to two nitrile groups in terms of its ability to support the multiple substitutions described herein. In the pioneering work on nucleophilic addition reactions to (η^6-arene)tricarbonyl chromium(0) complexes, the tricarbonylchromium(0) group was equated to a *para* group.[17]

Experimental

All reactions were performed under an inert atmosphere of dry nitrogen, using standard vacuum line and Schlenk-tube techniques.[18] Tetrahydrofuran was distilled over sodium benzophenone ketyl. Diisopropylamine was distilled and stored over KOH pellets. The concentration of methyllithium was determined by titration against diphenylacetic acid in THF.[19] Melting points were recorded in open capillaries on a Buchi 510 melting point apparatus, and are uncorrected. Infra-red spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer. NMR spectra were recorded at room temperature on a Bruker AM 360 instrument in CDCl$_3$ unless otherwise stated. Chemical shifts are reported in ppm relative to residual undeuterated solvent as the reference and *J* values are reported in Hz. Mass spectra were recorded on a JEOL AX 505W mass spectrometer and all elemental analyses were performed by the North London University microanalytical services. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh). Complexes 1a,[9d] 1b,[20] 1c,[21] 4,[20] 7,[13] 9[17a] and 11[22] were prepared according to literature procedures.

General procedure for trisubstitution using LiTMP

To a stirred solution of 2,2,6,6-tetramethylpiperidine (0.17 cm^3,

1.0 mmol) in THF (2 cm^3) cooled to −78 °C, MeLi (0.62 cm^3 of a 1.6 M solution in hexanes, 1.0 mmol) was added dropwise. The resulting solution temperature was then raised to 0 °C and stirred for 0.5 h and then recooled back to −78 °C. A solution of the complex (0.3 mmol) in degassed THF (4 cm^3) was then added and the reaction mixture stirred for 2 h at −78 °C. Me$_3$SiCl (0.2 cm^3, 1.1 mmol) was then added to this solution and the reaction was allowed to reach room temperature. The solvent was evaporated under reduced pressure. Flash column chromatography led to the isolation of the products.

[η^6-1-(*tert*-Butylsulfonyl)-2,4,6-tris(trimethylsilyl)benzene]tricarbonylchromium(0)[9d] 2a. Complex 1a (100 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at −78 °C for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the title complex 2a in 51% yield. Orange crystals; mp: 192–193 °C (Found C, 47.8; H, 6.8. C$_{22}$H$_{38}$CrO$_5$SSi$_3$ requires C, 47.97; H, 6.95%); ν_{max}(CHCl$_3$)/cm^{-1} 1977 (CO) and 1915 (CO); δ_H (360 MHz) 0.30 (s, 9H, Si(CH$_3$)$_3$), 0.53 (s, 18H, 2 × Si(CH$_3$)$_3$), 1.33 (s, 9H, C(CH$_3$)$_3$), 6.09 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) 5.3 (Si(CH$_3$)$_3$), 27.0 (C(CH$_3$)$_3$), 64.3 (C(CH$_3$)$_3$), 96.2 (ArC), 99.3 (ArC), 107.1 (ArC), 124.2 (ArC), 232.0 (Cr(CO)$_3$); *m/z* (EI, 70 eV) 550 (M$^+$, 1%), 466 (M − 3CO, 4), 73 (SiC$_3$H$_9$, 100).

[η^6-2,4,6-Tris(trimethylsilyl)anisole]tricarbonylchromium(0) 2b. Complex 1b (71 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at −78 °C for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* 2b in 42% yield along with complex 3b in 9% yields respectively. Yellow solid; mp: 195–196 °C (Found C, 49.4; H, 7.0. C$_{19}$H$_{32}$CrO$_4$Si$_3$ requires C, 49.53; H, 7.00%); ν_{max}(CHCl$_3$)/cm^{-1} 1980 (CO) and 1900 (CO); δ_H (360 MHz) 0.25 (s, 9H, Si(CH$_3$)$_3$), 0.37 (s, 18H, 2 × Si(CH$_3$)$_3$), 3.73 (s, 3H, OCH$_3$), 5.58 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) −0.9 (Si(CH$_3$)$_3$), 0.5 (Si(CH$_3$)$_3$), 63.5(OCH$_3$), 91.9 (2 × ArC), 96.0 (ArC), 106.1 (3 × ArC), 233.9 (CO); *m/z* (EI, 70 eV) 460 (M$^+$, 4%), 376 (M − 3CO, 12), 73 (SiC$_3$H$_9$, 100).

[η^6-2,5-Bis(trimethylsilyl)anisole]tricarbonylchromium(0)[9e] 3b. Yellow solid; mp: 101–102 °C (Found C, 48.5; H, 6.3. C$_{16}$H$_{24}$CrO$_4$Si$_2$ requires C, 48.48; H, 6.18%); ν_{max}(CHCl$_3$)/cm^{-1} 1980 (CO) and 1900 (CO); δ_H (360 MHz) 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.32 (s, 9H, Si(CH$_3$)$_3$), 3.72 (s, 3H, OCH$_3$), 4.70 (d, 1H, *J* 6, ArH), 4.84 (s, 1H, ArH), 5.57 (d, 1H, *J* 6, ArH); δ_C (90.5 MHz, CDCl$_3$) −6.3 (Si(CH$_3$)$_3$), −1.5(Si(CH$_3$)$_3$), 55.2 (OCH$_3$), 89.1 (ArC), 89.8 (2 × ArC), 95.2 (ArC), 102.4 (ArC), 104.1 (ArC), 233.8 (Cr(CO)$_3$); *m/z* (EI, 70 eV) 388 (M$^+$, 23%), 73 (SiC$_3$H$_9$, 100).

[η^6-2,4,6-Tris(trimethylsilyl)-*N,N*-dimethylbenzylamine]tricarbonylchromium(0) 2c. Complex 1c (81 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at −78 °C for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* 2c along with *complex* 3c in 40% and 48% yields respectively. Yellow solid; mp: 128–129 °C (Found C, 51.8; H, 7.7; N, 2.7. C$_{21}$H$_{37}$CrNO$_3$Si$_3$ requires C, 51.71; H, 7.65; N, 2.87%); ν_{max}(CHCl$_3$)/cm^{-1} 1970 (CO) and 1900 (CO); δ_H (360 MHz) 0.27 (s, 9H, Si(CH$_3$)$_3$), 0.32 (s, 18H, 2 × Si(CH$_3$)$_3$), 2.15 (s, 6H, 2 × CH$_3$), 3.38 (s, 2H, CH$_2$), 5.71 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) −1.0 (Si(CH$_3$)$_3$), 1.2 (Si(CH$_3$)$_3$), 44.5 (CH$_3$), 61.9 (CH$_2$), 97.3 (ArC), 98.2 (2 × ArC), 107.5 (3 × ArC), 234.3 (Cr(CO)$_3$); *m/z* (EI, 70 eV) 487 (M$^+$, 2%), 403 (M − 3CO, 36), 73 (SiC$_3$H$_9$, 100).

[η^6-2,5-Bis(trimethylsilyl)-*N,N*-dimethylbenzylamine]tricarbonylchromium(0) 3c. Yellow oil (Found C, 51.9; H, 6.8; N, 3.3. C$_{18}$H$_{29}$CrNO$_3$Si$_2$ requires C, 52.08; H, 6.97; N, 3.37%); ν_{max}(CHCl$_3$)/cm^{-1} 1970 (CO) and 1900 (CO); δ_H (360 MHz) 0.31 (s, 9H, Si(CH$_3$)$_3$), 0.36 (s, 9H, Si(CH$_3$)$_3$), 2.19 (s, 6H,

$2 \times CH_3$), 2.78 (d, 1H, J 13, CH_2), 3.52 (d, 1H, J 13, CH_2), 5.16 (d, 1H, J 6, ArH), 5.25 (s, 1H, ArH), 5.37 (d, 1H, J 6, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.3 (Si(CH_3)$_3$), 1.5 (Si(CH_3)$_3$), 45.2 (CH_3), 63.1 (CH_2), 96.1 (ArC), 97.8 (ArC), 98.2 (ArC), 99.1 (ArC), 104.4 (ArC), 107.1 (ArC), 233.9 (Cr(CO)$_3$); m/z (EI, 70 eV) 415 (M$^+$, 42%), 359 (M $-$ 2CO, 15), 73 (SiC$_3$H$_9$, 100).

[η^6-1,3,5-Tris(trimethylsilyl)benzene]tricarbonylchromium(0) 5a.

Complex **4** (64 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* **5a** along with **6a** in 26% and 63% yields respectively. Yellow solid; mp: 186–187 °C (Found C, 50.0; H, 6.9. C$_{18}$H$_{30}$CrO$_3$Si$_3$ requires C, 50.20; H, 7.02%); v_{max}(CHCl$_3$)/cm^{-1} 1938 (CO) and 1882 (CO); δ_H (360 MHz) 0.28 (s, 27H, $3 \times$ Si(CH$_3$)$_3$), 5.56 (s, 3H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.0 (Si(CH_3)$_3$), 97.6 (ArC), 105.4 (ArC), 234.0 (Cr(CO)$_3$); m/z (EI, 70 eV) 430 (M$^+$, 2%), 346 (M $-$ 3CO, 17), 73 (SiC$_3$H$_9$, 100).

[η^6-1,4-Bis(trimethylsilyl)benzene]tricarbonylchromium(0)[11] 6a.

Yellow solid; mp: 122–123 °C (Found C, 50.1; H, 6.1. C$_{15}$H$_{22}$CrO$_3$Si$_2$ requires C, 50.25; H, 6.19%); v_{max}(CHCl$_3$)/cm^{-1} 1970 (CO) and 1900 (CO); δ_H (360 MHz) 0.30 (s, 18H, $2 \times$ Si(CH$_3$)$_3$), 5.27 (s, 4H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.5 (Si(CH_3)$_3$), 97.3 (ArC), 101.9 (ArC), 233.4 (Cr(CO)$_3$); m/z (EI, 70 eV) 358 (M$^+$, 8%), 274 (M $-$ 3CO, 33), 73 (SiC$_3$H$_9$, 100).

General procedure using LDA

To a stirred solution of diisopropylamine (0.14 cm^3, 1.0 mmol) in THF (2 cm^3) cooled to $-78\,°C$, MeLi (0.62 cm^3 of a 1.6 M solution in hexanes, 1.0 mmol) was added dropwise. The resulting solution temperature was then raised to 0 °C and stirred for 0.5 h and then recooled back to $-78\,°C$. A solution of the complex (0.3 mmol) in degassed THF (4 cm^3) was then added and the reaction mixture stirred for 2 h at $-78\,°C$. Me$_3$SiCl (0.2 cm^3, 1.1 mmol) was then added to this solution and the reaction was allowed to reach room temperature. The solvent was evaporated under reduced pressure. Flash column chromatography led to the isolation of the products.

[η^6-3,5-Bis(trimethylsilyl)ethylbenzene]tricarbonylchromium(0) 8.

Complex **7** (71 mg, 0.3 mmol) was treated with LDA (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* **8** in 93% yield. Yellow solid; mp: 131–132 °C (Found C, 52.9; H, 6.5. C$_{17}$H$_{26}$CrO$_3$Si$_2$ requires C, 52.83; H, 6.78%); v_{max}(CHCl$_3$)/cm^{-1} 1940 (CO) and 1878 (CO); δ_H (360 MHz) 0.31 (s, 18H, $2 \times$ Si(CH$_3$)$_3$), 1.22 (t, 3H, J 7.6, CH$_3$), 2.36 (q, 2H, J 7.6, CH$_2$), 5.39 (s, 1H, ArH), 5.53 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.1 (Si(CH_3)$_3$), 15.5 (CH_3), 27.9 (CH_2), 98.1 (ArC), 101.1 (ArC), 103.8 (ArC), 111.5 (ArC), 234.0 (Cr(CO)$_3$); m/z (EI, 70 eV) 386 (M$^+$, 1%), 330 (M $-$ 2CO, 11), 73 (SiC$_3$H$_9$, 100).

[η^6-3,5-Bis(trimethylsilyl)toluene]tricarbonylchromium(0) 10.

Complex **9** (68 mg, 0.3 mmol) was treated with LDA (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* **10** in 95% yield. Yellow solid; mp: 150–151 °C (Found C, 51.5; H, 6.6. C$_{17}$H$_{24}$CrO$_3$Si$_2$ requires C, 51.61; H, 6.45%); v_{max}(CHCl$_3$)/cm^{-1} 1970 (CO) and 1900 (CO); δ_H (360 MHz) 0.20 (s, 18H, $2 \times$ Si(CH$_3$)$_3$), 1.75 (s, 3H, CH$_3$), 5.23 (s, 1H, ArH), 5.30 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.1 (Si(CH_3)$_3$), 26.6 (CH_3), 99.3 (ArC), 99.9 (ArC), 102.3 (ArC), 110.4 (ArC), 234.5 (Cr(CO)$_3$); m/z (EI, 70 eV) 372 (M$^+$, 3%), 288 (M $-$ 3CO, 8), 73 (SiC$_3$H$_9$, 100)

[η^6-3,5-Bis(trimethylsilyl)cyanomethylbenzene]tricarbonylchromium(0) 12.

Complex **11** (76 mg, 0.3 mmol) was treated with LDA (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Me$_3$SiCl (0.2 cm^3, 1.1 mmol) and subsequent work up provided the *title complex* **12** in 89% overall yield. Yellow oil (Found C, 51.1; H, 5.9; N, 3.50. C$_{17}$H$_{23}$CrNO$_3$Si$_2$ requires C, 51.38; H, 5.79; N, 3.52%); v_{max}(CHCl$_3$)/cm^{-1} 2250 (CN), 1980 (CO) and 1910 (CO); δ_H (360 MHz) 0.31 (s, 18H, $2 \times$ Si(CH$_3$)$_3$), 3.46 (s, 2H, CH$_2$), 5.40 (s, 1H, ArH), 5.58 (s, 2H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.1 (Si(CH_3)$_3$), 23.5 (CH_2), 96.0 (ArC), 97.9 (ArC), 99.8 (ArC), 103.8 (ArC), 232.2 (Cr(CO)$_3$); m/z (EI, 70 eV) 397 (M$^+$, 9%), 313 (M $-$ 3CO, 16), 73 (SiC$_3$H$_9$, 100).

[η^6-1,3,5-Tris(trimethylstannyl)benzene]tricarbonylchromium(0) 13a.

Complex **4** (64 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Me$_3$SnCl (218 mg, 1.1 mmol) and subsequent work up provided the *title complex* **13a** and **14a** in 58% and 7% yields respectively. Yellow solid; mp: 175–176 °C (Found: C, 30.5; H, 4.4. C$_{18}$H$_{30}$CrO$_3$Sn$_3$ requires C, 30.78; H, 4.28%); v_{max}(CHCl$_3$)/cm^{-1} 1956 (CO) and 1878 (CO); δ_H (360 MHz) 0.35 (s, 27H, $3 \times$ Sn(CH$_3$)$_3$), 5.35 (s, 3H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.0 (Sn(CH_3)$_3$), 102.6 (ArC), 105.4 (ArC), 234.0 (Cr(CO)$_3$); m/z (EI, 70 eV) 706 (M$^+$, 6%), 622 (M $-$ 3CO, 11), 73 (SiC$_3$H$_9$, 100).

[η^6-1,4-Bis(trimethylstannyl)benzene]tricarbonylchromium(0)[13] 14a.

Yellow oil (Found C, 33.6; H, 4.3. C$_{15}$H$_{22}$O$_3$CrSn$_2$ requires C, 33.33; H, 4.07%); v_{max}(CHCl$_3$)/cm^{-1} 1956 (CO) and 1880 (CO); δ_H (360 MHz) 0.21 (s, 18H, $2 \times$ Sn(CH$_3$)$_3$), 5.19 (s, 4H, ArH); δ_C (90.5 MHz, CDCl$_3$) -1.5 (Sn(CH_3)$_3$), 101.2 (ArC), 102.4 (ArC), 233.8 (Cr(CO)$_3$); m/z (EI, 70 eV) 540 (M$^+$, 33%), 458 (M $-$ 3CO, 39), 73 (SiC$_3$H$_9$, 100).

[η^6-1,3,5-Tris(diphenylphosphino)benzene]tricarbonylchromium(0) 13b.

Complex **4** (64 mg, 0.3 mmol) was treated with LiTMP (1.0 mmol) at $-78\,°C$ for 2 h. Addition of Ph$_2$PCl (0.20 cm^3, 1.1 mmol), subsequent work up followed by fractional crystallisation from acetone–hexane provided the *title complex* **13b** in 29% yield. Orange solid; mp: 173–174 °C (Found: C, 70.3; H, 4.5. C$_{45}$H$_{33}$CrO$_3$P$_3$ requires C, 70.50; H, 4.34%); v_{max} (CHCl$_3$)/cm^{-1} 1973 (CO) and 1903 (CO); δ_H (360 MHz; C$_3$D$_6$O) 5.15–5.18 (m, 3H, ArH), 7.29–7.46 (m, 30H, PhH); δ_C (90.5 MHz, C$_3$D$_6$O) 101.2 (ArC), 102.3 (ArC), 230.7 (Cr(CO)$_3$); δ_P (162 MHz, C$_3$D$_6$O) -4.38 (s, PPh$_2$); m/z (EI, 70 eV) 767 (M$^+$, 15%), 683 (M $-$ 3CO, 100).

Crystal data for 14a †

C$_{48}$H$_{39}$CrO$_4$P$_3$, M 824.70 g mol^{-1}, monoclinic, space group $P2_1/c$, $a = 20.7994(4)$, $b = 10.5200(3)$, $c = 19.6241(5)$ Å, $\beta = 103.703(1)°$, $V = 4171.72(18)$ Å^3, $Z = 4$, data collected 25 414, unique data used in refinement 9539, parameters 508, R_1 [$F^2 > 2\sigma(F^2)$] 0.0371, wR_2 (all data) 0.0893.

X-Ray crystallographic structure of 13b †

Crystals were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program[23] from 5 index frames of width 2° in ϕ using a Nonius ^{Kappa}CCD diffractometer, with a detector to crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5% completeness for $\theta = 27.5°$ using a combination of 2° ϕ and ω scans of 10–60 s deg^{-1} exposure time (depending on crystal quality). Crystals were indexed using the DENZO-SMN package[24] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[24]) resulted in unique data sets corrected for Lorentz and

polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97[25] and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97[25]) with the aid of the program XSeed.[26] In general all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except for acidic protons which were located on the final difference Fourier map and refined freely. All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM compatible PC.

Acknowledgements

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