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Regio- and diastereoselective formation of some (η^6-2-methylindoline)tricarbonylchromium(0) complex derivatives

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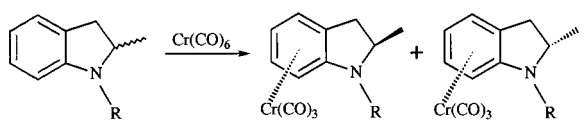
Abstract

Complexation of 2-methylindoline **1** and its derivatives **2** and **3** with $Cr(CO)_6$ gave complexes **4**–**9**. With the TIPS group attached to the nitrogen atom as in compound **3**, the complexation was completely diastereoselective producing the *endo* complex **9**. Treatment of the metallated complexes **8** and **9** with 2-halobenzoyl chlorides as electrophiles allowed for totally regioselective functionalisation at C(4), while the *exo* complex **6** was functionalised both at C(4) and C(7); with TMSCl and TIPSCl as electrophiles, the *endo* complex **9** also exhibited minor *exo* benzylic substitution to give **25** and **27**. Oxidative decomplexation of the indoline complexes efficiently releases the free 4-substituted indolines.

Keywords: Indolines; Arene complexes; Asymmetric synthesis; Chromium

1. Introduction

The indoline nucleus is present as an heterocyclic subunit in a wide range of natural products [1], in a number of medicinally relevant compounds [1,2], photo active devices, such as phototropic glass, non-linear optical materials [3], and some chiral indoline derivatives are excellent chiral catalysts for asymmetric syntheses [4]. The protecting group on the nitrogen has a strong influence upon the regiochemistry of indoline reactions as is described in the literature [5,6].



		Yield(%)	ratio		Yield(%)
[1] R=H	[4]	80	4:1	[5]	19
[2] R=Me	[6]	67	7:1	[7]	10
[3] R=TIPS	[8]	77*	—	[9]	63

Scheme 1. Reagents: $Cr(CO)_6$, dibutyl ether–THF (10:1). Only the relative stereochemistry indicated. *Complex **8** was obtained from **4**.

Tricarbonylchromium complexes are well known for deprotonation of the *exo* benzylic proton; thus, in α-methylbenzylmethylether, 1,3-dihydro-benzo[*c*]furan, indane and methylindoline tricarbonylchromium complexes, metallation occurs at the benzylic position [7a,d,8]. Introduction of substituents possessing a carbonyl functional group on the aromatic ring of indoline having the benzylic positions blocked was carried out by Oishi et al. using the chemistry of tricarbonylchromium complexes, but only poor regioselectivity was observed [9].

Due to the potential biological activity of indoline derivatives bearing carbonyl functional groups [1a,c,2a,e,f] there have been some attempts at their synthesis [la,6a,l0].

One possible approach, which is the subject of this paper, was envisaged utilising N-substituted (η^6-2-methylindoline)$Cr(CO)_3$ as building blocks for the synthesis of such indoline derivatives in which the steric demand of the methyl group at C(2) as well as the bulky nature of the group attached to the pyrrolidine nitrogen atom have a profound effect upon the course of the regio- and diastereoselectivity of those reactions.

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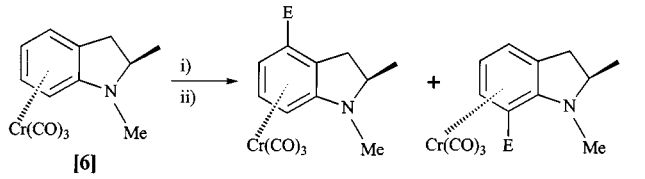
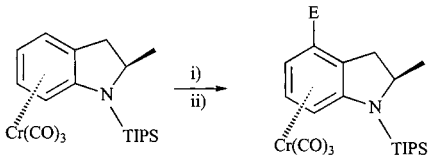


	Yied(%)		Yield(%)
E=2-FC_6H_4CO	[10] 22		[11] 24
E=2-ClC_6H_4CO	[12] 24		[13] 21
E=2-BrC_6H_4CO	[14] 29		[15] 25
Ratio	**1**	**:**	**1**

Scheme 2. Reagents: (i) *n*-BuLi (1.1 equivalents); (ii) $E^+ = 2\text{-}XC_6H_4COCl$ (X = F, Cl, Br).



	Yield(%)
E=2-FC_6H_4CO*	[16] 21
E=2-ClC_6H_4CO	[17] 23
E=2-BrC_6H_4CO*	[18] 28
E=TMS*	[19] 45
E=TIPS	[20] 32

Scheme 3. Reagents: (i) *n*-BuLi (2.5 equivalents)–TMEDA*; (ii) $E^+ = 2\text{-}XC_6H_4COCl$ (X = F, Cl, Br), TMSCl, TIPS.

Decomplexation of some complexes gave the corresponding stable substituted indolines.

2. Results and discussion

Complexation of **1** with $Cr(CO)_6$ gave a 8:1.8 separable diastereoisomeric mixture of the *exo* and *endo* complexes **4** and **5** in 80 and 19% yield, respectively (Scheme 1). The upfield signal of the C(2) methyl group in the ^{1}H-NMR spectrum of **4** is consistent with the *exo* complex and the downfield signal relative to the same group is in agreement with the *endo* complex **5** [9,11,12].

The predominance of **4** is consistent with the incoming chromium unit complexing preferentially to the less-hindered π face of the arene ring of **1** placing the methyl group at C(2) *anti* to the $Cr(CO)_3$ fragment [12e]. As expected, higher diastereoselectivity was observed on complexation when a bulky group was attached to the nitrogen atom [13a]. Methylation of **1** to **2** followed by complexation of **2** with the $Cr(CO)_6$ afforded the two separable *exo* and *endo* complexes **6** and **7** in 67 and 10% yield (ratio 7:1), respectively (Scheme 1). The ^{1}H-NMR spectra of complexes **6** and **7** showed the chemical shift of the C(2) methyl protons to be in agreement with those of complexes of **4** and **5**. Complexes **6** and **7** were also synthesised by methylation of **4** and **5**, respectively, and their spectroscopic data are in agreement with Pigge's data for these complexes obtained by a different route [12a]. The stereochemical assignment of **6** by X-ray analysis was also carried out by Pigge.

Treatment of the *exo* complex **6** with *n*-BuLi followed by quenching with an excess of various 2-X-benzoyl chlorides gave red solutions for the separable regioisomeric pairs: **10/11** (X = F), **12/13** (X = Cl) and **14/15** (X = Br) in 46, 45 and 54% yields (ratio 1:1), respectively. In all cases some starting material was recovered (Scheme 2).

The ^{1}H-NMR spectra of complexes **10**–**15** showed them to be unequivocally compatible with 4- and 7-substituted indoline complexes, with no benzylic substitution being detected. NOE difference spectroscopy of complex **15** with irradiation of the *N*-methyl protons at δ 2.80 resulted in enhancement of the methine proton, the methyl protons at C(2) and the aromatic protons of the electrophile. These observations are consistent with 7-substitution and therefore complex **14** must be the 4-substituted regioisomer. This conclusion was extended to all pairs of complexes shown in Scheme 2. Although complete regioselective functionalisation of the *exo* complex **6** was not attained, it should be stressed that our observation of lack of activation of the *exo* benzylic proton is in contrast with literature results for reactions with this type of complexes [7b,e,9,14a].

With these results in hand, a new strategy was undertaken for the regioselective synthesis of C(4) substituted 2-methylindolines. We turned to TIPS and TMS groups for N-protection of the indoline nitrogen on the basis that the steric hindrance caused by these bulky groups would enhance the regio- and diastereoselectivity of the corresponding complexes [12e,13b,c,14a]. The *endo* complex **9** was obtained from **5**, while the same reaction with TMSCl failed, which is quite usual when TMS is used as the protecting group for amines [15].

Alternatively, complex **9** could be generated as only one diastereoisomer by thermolysis of $Cr(CO)_6$ with compound **3** in 69% yield. The high diastereoselectivity of this reaction could presumably be due to the presence of the bulky TIPS group attached to the nitrogen atom of the indoline complex, which causes a hindered π face to the C(2) methyl group and to the $Cr(CO)_3$ fragment [14a,e]. Taking into account this last result, complex **8** could only be obtained from the *exo* complex **4**. The same reaction with TMSCl failed completely as was the case with **5** [15]. The distinction between the *exo* and *endo* complexes **8** and **9** was carried out by comparison with complexes **4** and **5**, and **6** and **7**, respectively, and with literature data [9,11,12,16].

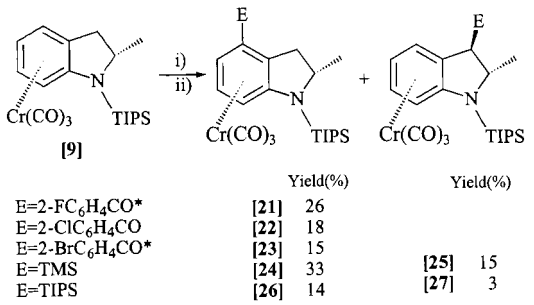
This was followed by treatment of the lithiated derivatives of complexes **8** and **9** with 2-halobenzoyl chlorides, TMSCl and TIPSCl (Schemes 3 and 4). Substitution at the 4-position was unequivocally observed

in all reactions and complexes **16**–**20** were obtained in moderate or modest yields (21–45%) besides some starting materials were also recovered. No traces of both benzylic and 7-substituted products were detected in the corresponding ^{1}H-NMR spectra. C-4 functionalisation was established by NOE difference spectroscopy of complex **19**. Irradiation of the protons of the TMS group at δ 0.36 ppm resulted in the enhancement of the H(5) signal and one of the benzylic protons signal at δ 2.46 ppm. Irradiation of the H(5) proton at δ 4.94 ppm produced an enhancement of the H(6) and TMS proton signals. Irradiation of the proton H(7) at δ 5.20 ppm produced an enhancement of the H(6) and TMS proton signals. This conclusion was extended to the other electrophiles of Scheme 3.

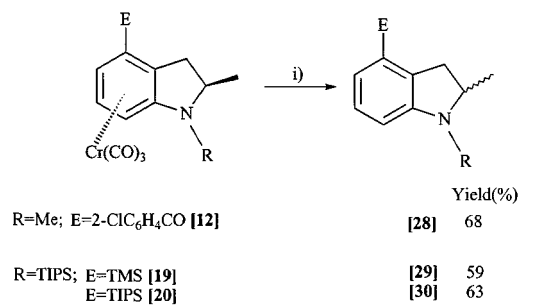
Using TMSCl and TIPSCl as electrophiles (Scheme 4), traces of C(3)-substituted complexes were also observed (complexes **25** and **27**), indicating that the regiochemistry related to benzoyl group containing electrophiles does not transfer completely to electrophiles like TMSCl and TIPSCl. The presence of the methyl group at C(2) *endo* to the $Cr(CO)_3$ fragment in complex **9** would allow, to some extent, C(3) *exo* deprotonation and subsequent functionalisation presumably due to the least steric hindrance in relation to complex **8**. The C(4) functionalisation of **24** was established from NOE difference spectroscopy. Irradiation of the protons of the TMS group at δ 0.34 ppm resulted in the enhancement of the H(5) signal and irradiation of H(7) at δ 5.43 ppm produced an enhancement of the H(6) and TIPS proton signals. These observations were consistent with a 4-substituted indoline complex derivatives and this conclusion was extended to the other electrophiles reported in Scheme 4.

As was observed for the functionalisation of complexes **6**, **8** and **9** using 2-halobenzoyl chlorides as electrophiles there were no benzylic substituted byproducts formed, a result which contrasts the reactions using (η^6-fluorene)$Cr(CO)_3$ [13], the [η^6-(1,3-dihydrobenzo[*c*]furan)]$Cr(CO)_3$ [7d] and other complexes which possess one six-membered heterocyclic ring condensed to the aromatic ring [7d,13] where there are no stereoelectronic constraints. Our results differ with Oishi's conclusions [9] and those of Kalinin in which benzylic functionalisation on (*N*-methylindoline)tricarbonylchromium occurred [7a], presumably due to the use of a different metallating agent and the presence (in the present complexes) of the stereogenic centre at C(2). On the other hand, our results are in agreement with Simpkins's studies on the (1,3-dihydroisobenzofuran)tricarbonylchromium complex [7b].

Products **12**, **19** and **20** were subjected to known decomplexation procedures [17] in order to produce the corresponding non-complexed substituted indolines and to evaluate their stability for further studies in the enantiomerically pure series (Scheme 5).



Scheme 4. Reagents: (i) *n*-BuLi (2.5 equivalents)–TMEDA*; (ii) E^+ = 2-XC_6H_4COCl (X = F, Cl, Br), TMSCl, TIPSCl.



Scheme 5. (i) hν/O_2.

3. Concluding remarks

The presence of the methyl group in the stereogenic centre at C(2) of the pyrrolidine moiety has a pronounced effect on regio- and diastereoselectivity in the complexation of some indolines. It was shown that the *exo* complex **6**, is capable of undergoing exclusively C(4) and C(7) functionalisation. The choice of the TIPS bulky group attached to N(1) in compounds **8** and **9** afforded only one regioisomer upon reaction of their lithiated derivatives and absence of functionalisation at the benzylic position was observed with 2-halobenzoyl chlorides. When TMSCl and TIPSCl were used as electrophiles with the complexes **8** and **9**, only *exo* benzylic minor products were obtained for the lithiated derivative of **9**, presumably due to the absence of steric hindrance of the *endo* methyl group at C(2).

Thus, the high value of (arene) chromium chemistry for regio- and diastereoselective synthesis of this type of molecules in relation to free indolines has been demonstrated, in which the regioselective introduction of substituents possessing a carbonyl functional group are relevant.

4. Experimental

Melting points, Reichert Thermovar (uncorrected values); IR, Perkin–Elmer 1725X FT-IR; ^{1}H-NMR, General Electric QE (300 MHz) (Me_4Si at $\delta_H = 0.00$ as an internal standard and the spectra were recorded in $CHCl_3$-*d*); MS, Kratos MS 25 RF (electron impact or fast atom bombardment) and Extrell (Waters) FTMS 2001-DT STICR; Elemental analyses, Carlo Erba 1106; CC, Merck Kieselgel 60 (230–400 mesh); TLC, Merck silica gel precoated plates (60F-254) 0.5 or 2 mm for preparative chromatography.

All reactions involving tricarbonylchromium(0) complexes were carried out in Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures [18]. Unless otherwise stated, petrol refers to petroleum ether b.p. 40–60°C and ether refers to diethyl ether. The titration of *n*-BuLi was carried out using diphenylacetic acid as standard [19]. Organic extracts were dried over anhydrous magnesium sulphate. 1,2-Dimethylindoline (**2**) was not stable and consequently, good microanalytical data could not be obtained. In contrast, microanalytical data from its complexes *exo*- and *endo*-(η^6-1,2-dimethylindoline)tricarbonylchromium(0) (**6** and **7**), respectively, are correct.

4.1. General method for the preparation of N-substituted indolines

n-BuLi (1.2 equivalents) was added to a solution of 2-methylindoline (**1**) in THF at −78°C and stirred for 2 h. The chosen electrophile (methyl iodide or chlorotriisopropylsilane) was added, the mixture stirred for 1 h at −78°C and the solution allowed to react for 24 h at room temperature. Water–ether was added, the ether portion separated, dried and the solvent removed to afford a crude product, which was purified by flash chromatography (*n*-hexane) to yield compounds **2** and **3**.

4.1.1. 1,2-Dimethylindoline (2)

Prepared from 2-methylindoline (**1**) (1.0 ml, 7.68 mmol), *n*-BuLi (6.6 ml, 9.24 mmol) and methyl iodide (0.6 ml, 9.60 mmol) according to the general procedure to afford **2** as a yellow oil (890 mg, 79%). IR (cm^{-1}) ν_{max} (film): 3050 (C–H)Ar, 2959, 2931, 2871 (C–H), 1608, 1486, 1461 (C=C); ^{1}H-NMR: δ 1.31 (d, 3H, $J = 6.3$ Hz, CH_3), 2.58 (dd, 1H, $J = 10.2$ and 15.0 Hz, CH_2), 2.69 (s, 3H, NCH_3), 3.06 (dd, 1H, $J = 8.1$ and 15.0 Hz, CH_2), 3.38 (m, 1H, CH), 6.44 (d, 1H, $J = 7.5$ Hz, ArH), 6.65 (t, 1H, $J = 7.5$ Hz, ArH), 7.05 (m, 2H, ArH); MS (EI), *m*/*z* (%): 147 [M^+] (44), 132 (100), 117 (33).

4.1.2. 1-Triisopropylsilyl-2-methylindoline (3)

Prepared from 2-methylindoline (**1**) (1.0 ml, 7.68 mmol), *n*-BuLi (6.6 ml, 9.24 mmol) and chlorotriisopropylsilane (2.0 ml, 9.22 mmol) according to the general procedure to afford **3** as a colourless oil (1.48 g, 67%). IR (cm^{-1}) ν_{max} (film): 2946, 2875 (C–H), 1605, 1477 (C=C); ^{1}H-NMR: δ 1.03–1.18 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.32–1.44 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.50 (d, 1H, $J = 14.7$ Hz, CH_2), 3.20 (dd, 1H, $J = 8.7$ and 14.7 Hz, CH_2), 3.99 (m, 1H, CH), 6.64 (t, 1H, $J = 7.8$ Hz, ArH), 6.69 (d, 1H, $J = 7.8$ Hz, ArH), 6.95 (t, 1H, $J = 7.8$ Hz, ArH), 7.08 (d, 1H, $J = 7.8$ Hz, ArH); MS (EI), *m*/*z* (%): 289 [M^+] (21), 246 (100), 160 (6), 132 (6); Anal. Found: C, 74.64; H, 10.79; N, 4.80. Calc. for $C_{18}H_{31}NSi$ (289.54): C, 74.67; H, 10.79; N, 4.84%.

4.2. General methods for preparation of (η^6-N-substituted-2-methylindoline)-tricarbonylchromium(0) complexes

Procedure A: A mixture of a slight excess of indoline (2-methylindoline (**1**), 1,2-dimethylindoline (**2**) and 1-triisopropylsilyl-2-methylindoline (**3**)) and hexacarbonylchromium(0) in deoxygenated dibutyl ether (80 ml)–THF (8 ml) were heated under reflux for 48 h. The resulting solution was cooled, filtered through silica with ether and concentrated under reduced pressure to afford a crude product which was purified by column chromatography to yield complexes **4**–**7** and **9**.

Procedure B: A solution of (η^6-2-methylindoline)tricarbonylchromium(0) complex [**4** (*exo*) or **5** (*endo*)] in THF was added to a suspension of NaH (five equivalents) previously washed in *n*-hexane (50 ml). When no further gas was evolved, the mixture was cooled (0°C) and methyl iodide or chlorotriisopropylsilane was added. The reaction was stirred for 2 h at 0°C and 24 h at room temperature. Diethyl ether was added and the resulting solution filtered under vacuum through a silica column. When necessary the crude product was purified by column chromatography to yield complexes **6**–**9**.

4.2.1. exo-(η^6-2-Methylindoline)tricarbonylchromium(0) (4) and endo-(η^6-2-methylindoline)tricarbonylchromium(0) (5)

By procedure A: from 2-methylindoline (**1**) (2.0 ml, 15.37 mmol) and hexacarbonylchromium(0) (3.08 g, 14.02 mmol) to give after column chromatography (*n*-hexane–ether: 60:40) complexes **4** and **5**. Recrystallisation from ether–*n*-hexane gave yellow crystals in both cases. Following the order of elution: Complex **4** (2.95 g, 80%); m.p. 95–96°C; IR (cm^{-1}) ν_{max} (KBr): 3426 (N–H), 3092 (C–H)Ar, 2970, 2932 (C–H), 1942, 1861, 1833 (C≡O), 1562, 1471 (C=C); ^{1}H-NMR: δ 1.33 (d,

3H, $J = 6.3$ Hz, CH_3), 2.51(dd, 1H, $J = 10.8$ and 15.0 Hz, CH_2), 2.90 (dd, 1H, $J = 7.8$ and 15.0 Hz, CH_2), 3.70 (s, 1H, NH), 4.11 (m, 1H, CH), 4.82 (t, 1H, $J = 6.3$ Hz, ArH), 4.90 (d, 1H, $J = 6.3$ Hz, ArH), 5.38 (t, 1H, $J = 6.3$ Hz, ArH), 5.57 (d, 1H, $J = 6.3$ Hz, ArH); MS (EI), m/z (%): 269 [M^+] (7), 213 (5), 185 (31), 133 (36), 118 (100), 103 (5); Anal. Found: C, 53.36; H, 4.10; N, 5.16. Calc. for $C_{12}H_{11}CrNO_3$ (269.22): C, 53.54; H, 4.12; N, 5.20%. Complex **5** (693 mg, 19%); m.p. 139–140°C; IR (cm^{-1}) ν_{max} (KBr): 3426 (N–H), 3076 (CH)Ar, 2967, 2928, 2859 (C–H), 1937, 1868, 1827 (C≡O), 1567, 1481 (C=C); ^{1}H-NMR: δ 1.43 (d, 3H, $J = 6.3$ Hz, CH_3), 2.64 (dd, 1H, $J = 3.9$ and 15.8 Hz, CH_2), 3.18 (dd, 1H, $J = 10.2$ and 15.8 Hz, CH_2), 3.44 (s, 1H, NH), 4.03 (m, 1H, CH), 4.84 (t, 1H, $J = 6.3$ Hz, ArH), 4.95 (d, 1H, $J = 6.3$ Hz, ArH), 5.36 (t, 1H, $J = 6.3$ Hz, ArH), 5.59 (d, 1H, $J = 6.3$ Hz, ArH). MS (EI), m/z (%): 269 [M^+] (13), 213 (9), 185 (52), 133 (36), 118 (100), 103 (4); Anal. Found: C, 53.46; H, 4.11; N, 5.04. Calc. for $C_{12}H_{11}CrNO_3$ (269.22): C, 53.54; H, 4.12; N 5.20%.

4.2.2. exo-(η^6-1,2-Dimethylindoline)tricarbonylchromium(0) (**6**)

By procedure B: from **4** (630 mg, 2.34 mmol) in THF (15 ml), NaH (323 mg, 10.75 mmol) and methyl iodide (0.70 ml, 11.24 mmol). Column chromatography (petrol–ether: 70:30) and recrystallisation from ether–*n*-hexane gave **6** as yellow crystals (512 mg, 77%); m.p. 113–115°C; IR (cm^{-1}) ν_{max} (KBr): 3079 (C–H)Ar, 2967, 2927, 2854 (C–H), 1935, 1863, 1834 (C≡O), 1552, 1482 (C=C); ^{1}H-NMR: δ 1.31 (d, 3H, $J = 6.0$ Hz, CH_3), 2.51(dd, 1H, $J = 10.8$ and 15.0 Hz, CH_2), 2.62 (s, 3H, NCH_3), 2.91 (dd, 1H, $J = 7.8$ and 15.0 Hz, CH_2), 3.52 (m, 1H, CH), 4.71 (d, 1H, $J = 6.0$ Hz, ArH) 4.87 (t, 1H, $J = 6.0$ Hz, ArH), 5.36 (t, 1H, $J = 6.0$ Hz, ArH), 5.52 (d, 1H, $J = 6.0$ Hz, ArH); MS (EI), m/z (%): 283 [M^+] (11), 227 (7), 199 (42), 147 (39), 132 (100), 117 (33), 103 (5); Anal. Found: C, 54.94; H, 4.60; N, 4.76. Calc. for $C_{13}H_{13}CrNO_3$ (283.25): C, 55.13; H, 4.63; N, 4.95%.

4.2.3. endo-(η^6-1,2-Dimethylindoline)tricarbonylchromium(0) (**7**)

By procedure B: from **5** (339 mg, 1.26 mmol), NaH (0.15 g, 5.00 mmol) and methyl iodide (0.35 ml, 5.60 mmol). Recrystallisation from ether–petrol gave yellow crystals (335 mg, 93%); m.p. 141–143°C; IR (cm^{-1}) ν_{max} (KBr): 3100 (C–H)Ar, 2926 (C–H), 1931, 1847, 1827 (C≡O), 1560, 1497, 1456 (C=C); ^{1}H-NMR: δ 1.40 (d, 3H, $J = 6.0$ Hz, CH_3), 2.62 (dd, 1H, $J = 4.0$ and 15.6 Hz, CH_2), 2.74 (s, 3H, NCH_3), 3.17 (dd, 1H, $J = 9.9$ and 15.6 Hz, CH_2), 3.87 (m, 1H, CH), 4.78 (m, 2H, ArH), 5.40 (t, 1H, $J = 6.3$ Hz, ArH), 5.59 (d, 1H, $J = 6.3$ Hz, ArH); MS (EI), m/z (%): 283 [M^+] (1), 227 (1), 199 (3), 147 (32), 132 (100), 117 (35), 103 (7); Anal. Found: C, 54.98; H, 4.71; N, 4.68. Calc. for $C_{13}H_{13}CrNO_3$ (283.25): C, 55.13; H, 4.63; N 4.95%.

4.2.4. exo-(η^6-1,2-Dimethylindoline)tricarbonylchromium(0) (**6**) and endo-(η^6-1,2-dimethylindoline)tricarbonylchromium(0) (**7**)

By procedure A: from 1,2-dimethylindoline (**2**) (828 mg, 5.63 mmol) and hexacarbonylchromium(0) (1.32 g, 5.99 mmol); Column chromatography (*n*-hexane–ether: 70:30) gave complexes **6** and **7**. Following the order of elution: complex **6** (1.03 g, 67%) and complex **7** (153 mg, 10%). Recrystallisation from ether–*n*-hexane gave yellow crystals in both cases whose spectroscopic properties are in agreement with previous results.

4.2.5. exo-(η^6-1-Triisopropylsilyl-2-methylindoline)tricarbonylchromium(0) (**8**)

By procedure B: from **4** (1.14 g, 4.34 mmol) in THF (50 ml), NaH (470 mg, 15.66 mmol) and chlorotriisopropylsilane (2.0 ml, 9.35 mmol). Recrystallisation from ether–*n*-hexane gave yellow crystals (1.42 g, 77%); m.p. 75–76°C; IR (cm^{-1}) ν_{max} (KBr): 3093 (C–H)Ar, 2950, 2870 (C–H), 1952, 1859 (C≡O), 1543, 1445 (C=C); ^{1}H-NMR: δ 1.05–1.25 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.36–1.43 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.46 (d, 1H, $J = 15.3$ Hz, CH_2), 3.45 (dd, 1H, $J = 9.0$ and 15.3 Hz, CH_2), 4.13 (m, 1H, CH), 4.92 (t, 1H, $J = 6.0$ Hz, ArH), 5.06 (d, 1H, $J = 6.0$ Hz, ArH), 5.17 (t, 1H, $J = 6.0$ Hz, ArH), 5.58 (d, 1H, $J = 6.0$ Hz, ArH); MS (EI), m/z (%): 425 [M^+] (15), 369 (4), 341(100), 289 (15), 246 (61), 160 (4), 132 (4); Anal. Found: C, 59.48; H, 7.44; N, 3.47; Calc. for $C_{21}H_{31}CrO_3Si$ (425.57): C, 59.27; H, 7.34; N, 3.29%.

4.2.6. endo-(η^6-1,2-Triisopropylsilyl-2-methylindoline)tricarbonylchromium(0) (**9**)

By procedure B: from **5** (399 mg, 1.48 mmol) in THF (50 ml), NaH (224 mg, 7.45 mmol) and chlorotriisopropylsilane (1.6 ml, 7.48 mmol). Recrystallisation from ether–*n*-hexane gave **9** as yellow crystals (399 mg, 63%); m.p. 135–136°C; IR (cm^{-1}) ν_{max} (KBr): 2947, 2868 (CH), 1955, 1844 (C≡O), 1540, 1459 (C=C); ^{1}H-NMR: δ 1.06–1.25 (m, 18H, $Si[CH(CH_3)_2]_3$), 1.33–1.40 (m, 3H, $Si[CH(CH_3)_2]_3$), 1.47 (3H, d, $J = 6.6$ Hz, CH_3), 2.46 (d, 1H, $J = 15.6$ Hz, CH_2), 3.18 (dd, 1H, $J = 9.3$ and 15.6 Hz, CH_2), 4.00 (m, 1H, CH), 4.85 (t, 1H, $J = 6.3$ Hz, ArH), 5.25 (d, 1H, $J = 6.3$ Hz, ArH), 5.33 (t, 1H, $J = 6.3$ Hz, ArH), 5.51 (d, 1H, $J = 6.3$ Hz, ArH). MS (EI), m/z (%): 425 [M^+] (15), 369 (10), 341 (100), 289 (21), 246 (83), 160 (5), 132 (5); Anal. Found: C, 59.46; H, 7.46; N, 3.31. Calc. for $C_{21}H_{31}CrO_3Si$ (425.57): C, 59.27; H, 7.34; N, 3.29%. *By procedure A:* from 1-triisopropylsilyl-2-methylindoline (**3**) (4.27 g, 14.76 mmol) and hexacarbonylchromium(0) (3.20 g, 14.54 mmol). Column chromatography (*n*-hexane–ether: 80:20) gave the complex **9** (4.30 g, 69%). Recrystallisation from ether–*n*-hexane gave yellow crystals,

whose spectroscopic properties are in agreement with the previous result.

4.3. General method for lithiation of exo-(η⁶-1,2-dimethylindoline)tricarbonylchromium(0) and electrophilic additions

n-BuLi (1.1 equivalents) was added to a solution of *exo*-(η⁶-1,2-dimethylindoline) tricarbonylchromium(0) (**6**) in THF at −78°C and stirred for 3 h. The chosen electrophile was added, the mixture stirred for 2 h at −78°C and the solution allowed to react for 20 h at room temperature. The solution was washed with water, the aqueous layer was extracted with ether and the organic phases combined, dried, concentrated and purified by column chromatography (petrol–ether: 70:30) to yield compounds **10**–**15**.

4.3.1. exo-[η⁶-1,2-Dimethyl-4-(2′-fluorobenzoyl)-indoline]tricarbonylchromium(0) (**10**) and exo-[η⁶-1,2-dimethyl-7-(2′-fluorobenzoyl)indoline]-tricarbonylchromium(0) (**11**)

From **6** (221 mg, 0.78 mmol), *n*-BuLi (0.55 ml, 0.88 mmol) and 2-fluorobenzoyl chloride (0.75 ml, 6.32 mmol). Purification by column chromatography afforded complexes **10** and **11**. Recrystallisation from ether–petrol gave red crystals in both cases. Complex **10**: (69 mg, 22%); m.p. 100–103°C; IR (cm^{-1}) ν_{max} (film): 2971 (C–H), 1955, 1872 (C≡O), 1665 (C=O), 1612, 1543, 1515, 1483, 1452 (C=C); ^{1}H-NMR: δ 1.34 (d, 3H, $J = 6.0$ Hz, CH_3), 2.61 (s, 3H, NCH_3), 2.70 (dd, 1H, $J = 10.5$ and 16.3 Hz CH_2), 3.37 (m, 1H, CH), 3.54 (dd, 1H, $J = 7.8$ and 16.3 Hz, CH_2), 5.00 (d, 1H, $J = 6.6$ Hz, ArH) 5.21(t, 1H, $J = 6.6$ Hz, ArH), 5.29 (d, 1H, $J = 6.6$ Hz, ArH), 7.15–8.08 (m, 4H, Ar′H); MS (EI), m/z (%): 405 [M^+] (12), 349 (12), 321(55), 269 (5), 250 (9), 123 (100); Anal. Found: C, 59.37; H, 4.00; N, 3.55. Calc. for $C_{20}H_{16}CrFNO_4$ (405.35): C, 59.26; H, 3.98; N, 3.46%. Complex **11** (76 mg, 24%); m.p. 112–114°C; IR (cm^{-1}) ν_{max} (film): 2966 (C–H), 1958, 1883, 1860 (C≡O), 1655 (C=O), 1615, 1559, 1521, 1489, 1466, 1457 (C=C); ^{1}H-NMR: δ 1.33 (d, 3H, $J = 6.3$ Hz, CH_3), 2.58 (s, 3H, NCH_3), 2.62 (dd, 1H, $J = 10.5$ and 15.6 Hz, CH_2), 3.06 14 (dd, 1H, $J = 8.4$ and 15.6 Hz, CH_2), 3.72 (m, 1H, CH), 4.81 (t, 1H, $J = 6.3$ Hz, ArH), 5.33 (d, 1H, $J = 6.3$ Hz, ArH), 5.71 (d, 1H, $J = 6.3$ Hz, ArH), 7.12–7.89 (m, 4H, Ar′H); MS (EI), m/z (%): 405 [M^+] (5), 349 (8), 321 (32), 269 (17), 250 (25), 123 (100); Anal. Found: C, 59.61; H, 4.03; N, 3.36. Calc. for $C_{20}H_{16}CrFNO_4$ (405.35): C, 59.26; H, 3.98; N, 3.46%.

4.3.2. exo-[η⁶-1,2-Dimethyl-4-(2′-chlorobenzoyl)-indoline]tricarbonylchromium(0) (**12**) and exo-[η⁶-1,2-dimethyl-7-(2′-chlorobenzoyl)indoline]-tricarbonylchromium(0) (**13**)

From **6** (332 mg, 1.17 mmol), *n*-BuLi (1.0 ml, 1.30 mmol) and 2-chlorobenzoyl chloride (0.75 ml, 5.86 mmol). After purification by column chromatography the ^{1}H-NMR spectrum showed a mixture of two compounds in the ratio 1:1. Separation by recrystallisation from ether–petrol afforded complexes **12** (red oil) and **13** (red crystals). Complex **12**: (119 mg, 24%); IR (cm^{-1}) ν_{max} (film): 2973, 2868 (C–H), 1955, 1869 (C≡O), 1654 (C=O), 1592, 1559, 1541, 1474 (C=C); ^{1}H-NMR: δ 1.33 (d, 3H, $J = 5.7$ Hz, CH_3), 2.58 (s, 3H, NCH_3), 2.70 (m, 1H, CH_2), 3.23–3.42 (m, 2H, CH_2 and CH), 5.05 (d, 1H, $J = 6.6$ Hz, ArH) 5.17 (t, 1H, $J = 6.6$ Hz, ArH), 5.27 (d, 1H, $J = 6.6$ Hz, ArH), 7.36–8.04 (m, 4H, Ar′H); MS (EI), m/z (%): 423 (5), 421 [M^+] (12), 367 (5), 365 (12), 339 (6), 337 (15), 287 (3), 285 (9), 250 (100), 141 (12), 139 (35); HRMS (EI) Found: 421.0175. Calc. for $C_{20}H_{16}CrClNO_4$: 421.0173. Complex **13**: (104 mg, 21%); m.p. (dec.) 153–154°C; IR (cm^{-1}) ν_{max} (film): 3096 (C–H)Ar, 2970, 2938 (C–H), 1957, 1885, 1862 (C≡O), 1657 (C=O), 1588, 1537, 1475 (C=C); ^{1}H-NMR: δ 1.37 (d, 3H, $J = 6.0$ Hz, CH_3), 2.63 (dd, 1H, $J = 10.2$ and 15.3 Hz, CH_2), 2.77 (s, 3H, NCH_3), 3.08 (dd, 1H, $J = 8.7$ and 15.3 Hz, CH_2), 3.79 (m, 1H, CH), 4.76 (t, 1H, $J = 6.3$ Hz, ArH), 5.46 (d, 1H, $J = 6.3$ Hz, ArH), 5.77 (d, 1H, $J = 6.3$ Hz, ArH), 7.38–7.74 (m, 4H, Ar′H); MS (EI), m/z (%): 421 [M^+] (1), 365 (1), 337 (4), 287 (9), 285 (26), 250 (39), 141 (33), 139 (100); Anal. Found: C, 56.93; H, 3.90; N, 3.32. Calc. for $C_{20}H_{16}CrC1NO_4$ (421.80): C, 56.95; H, 3.82; N 3.32%.

4.3.3. exo-[η⁶-1,2-Dimethyl-4-(2′-bromobenzoyl)-indoline]tricarbonylchromium(0) (**14**) and exo-[η⁶-1,2-dimethyl-7-(2′-bromobenzoyl)indoline]-tricarbonylchromium(0) (**15**)

From **6** (361 mg, 1.28 mmol), *n*-BuLi (1.1 ml, 1.43 mmol) and 2-bromobenzoyl chloride (0.84 ml, 6.38 mmol). After purification by column chromatography the ^{1}H-NMR spectrum showed a mixture of two compounds in the ratio 1:1. Separation was carried out by recrystallisation from ether–petrol to afford complexes **14** (red oil) and **15** (red crystals). Complex **14**: (170 mg, 29%); IR (cm^{-1}) ν_{max} (film): 2963, 2926, 2862 (C–H), 1957, 1877 (C≡O), 1669 (C=O), 1541,1508, 1457 (C=C); ^{1}H-NMR: δ 1.33 (d, 3H, $J = 5.7$ Hz, CH_3), 2.59 (s, 3H, NCH_3), 2.71 (m, 1H, CH_2), 3.23–3.43 (m, 2H, CH_2 and CH), 5.06 (d, 1H, $J = 6.6$ Hz, ArH), 5.16 (t, 1H, $J = 6.6$ Hz, ArH), 5.28 (d, 1H, $J = 6.6$ Hz, ArH), 7.33–7.62 (m, 4H, Ar′H); MS (EI), m/z (%): 468 (17), 467 (20), 466 (18), 465 [M^+] (17), 411 (20), 409 (20), 384 (16), 383 (37), 382 (21), 381 (36), 332 (11), 331 (16), 330 (22), 329 (16), 250 (100), 185 (60), 183 (60); HRMS (EI) Found: 464.9669. Calc. for $C_{20}H_{16}CrBrNO_4$: 464.9668. Complex **15**: (150 mg, 25%); m.p. 158°C; IR (cm^{-1}) ν_{max} (KBr): 3090 (C–H)Ar, 2968, 2930, 2855 (C–H), 1956, 1884, 1862 (C≡O), 1658 (C=O), 1585, 1537, 1474 (C=C); ^{1}H-NMR: δ 1.39 (d, 3H, $J = 6.0$ Hz, CH_3), 2.63 (dd, 1H, $J = 10.5$ and 15.5 Hz, CH_2), 2.80 (s, 3H, NCH_3),

3.08 (dd, 1H, $J = 8.7$ and 15.5 Hz, CH_2), 3.80 (m, 1H, CH), 4.76 (t, 1H, $J = 6.3$ Hz, ArH), 5.45 (d, 1H, $J = 6.3$ Hz, ArH), 5.78 (d, 1H, $J = 6.3$ Hz, ArH), 7.36–7.72 (m, 4H, Ar′H). MS (FAB), m/z (%): 467 (1), 465 [M^+] (1), 411 (1), 409 (1), 383 (5), 381 (7), 331 (7), 329 (8), 250 (100), 185 (27), 183 (30); Anal. Found: C, 51.44; H, 3.51; N, 2.74. Calc. for $C_{20}H_{16}CrBrNO_4$ (464.25): C, 51.52; H, 3.46; N 3.00%.

4.4. General method for lithiation of exo-(η⁶-1-triisopropylsilyl-2-methyl-indoline)-tricarbonylchromium(0) and electrophilic additions

n-BuLi (2.5 equivalents) was added to a solution of *exo* - (η⁶ - 1 - triisopropylsilyl - 2 - methylindoline)tricarbonylchromium(0) (**8**) in THF (with or without TMEDA) at −78°C and stirred for 3 h. The chosen electrophile was added, the mixture stirred for 1 h at −78°C and the solution allowed to react for 20 h at room temperature. The solution was washed with water, the aqueous layer was extracted with ether and the organic phases combined, dried, concentrated and purified by chromatography eluting with appropriate solvents system to yield compounds **16**–**20**.

4.4.1. exo-[η⁶-1-Triisopropylsilyl-2-methyl-4-(2′-fluorobenzoyl)indoline]tricarbonylchromium(0) (16)

From **8** (360 mg, 0.85 mmol) in THF (15 ml)–TMEDA (0.5 ml), *n*-BuLi (1.5 ml, 2.20 mmol) and 2-fluorobenzoyl chloride (0.5 ml, 4.22 mmol). Purification by column chromatography (*n*-hexane–ether: 75:25) and recrystallisation from ether–*n*-hexane afforded product **16** (98 mg, 21%) as red crystals; m.p. 123–124°C; IR (cm^{-1}) ν_{max} (film): 2951, 2869 (C–H), 1958, 1875 (C≡O), 1665 (C=O), 1612, 1581, 1524, 1453 (C=C); ^{1}H-NMR: δ 1.05–1.25 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.39–1.49 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.93 (d, 1H, $J = 17.4$ Hz, CH_2), 3.73 (dd, 1H, $J = 9.3$ and 17.4 Hz, CH_2), 4.20 (m, 1H, CH), 5.07 (t, 1H, $J = 6.6$ Hz, ArH), 5.25 (dd, 1H, $J = 2.4$ and 6.6 Hz, ArH), 5.30 (d, 1H, $J = 6.6$ Hz, ArH), 7.13–7.69 (m, 4H, Ar′H); MS (EI), m/z (%): 547 [M^+] (4), 463 (62), 411 (26), 392 (10), 368 (67), 123 (100); Anal. Found: C, 61.52; H, 6.43; N, 2.62. Calc. for $C_{28}H_{34}CrFNO_4Si$ (547.67): C, 61.41; H, 6.26; N, 2.56%.

4.4.2. exo-[η⁶-1-Triisopropylsilyl-2-methyl-4-(2′-chlorobenzoyl)indoline]tricarbonylchromium(0) (17)

From **8** (192 mg, 0.45 mmol) in THF (15 ml), *n*-BuLi (0.8 ml, 1.13 mmol) and 2-chlorobenzoyl chloride (0.3 ml, 2.26 mmol). Purification by column chromatography (petrol–ether: 80:20) and recrystallisation from ether–*n*-hexane afforded product **17** (59 mg, 23%) as red crystals; m.p. 128–130°C; IR (cm^{-1}) ν_{max} (film): 2952, 2870 (C–H), 1957, 1874 (C≡O), 1662 (C=O), 1592, 1524 (C=C); ^{1}H-NMR: δ 1.05–1.25 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.39–1.48 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.82 (d, 1H, $J = 17.1$ Hz, CH_2), 3.52 (dd, 1H, $J = 9.0$ and 17.1 Hz, CH_2), 4.14 (m, 1H, CH), 5.06 (t, 1H, $J = 6.6$ Hz, ArH), 5.27 (d, 1H, $J = 6.6$ Hz, ArH), 5.34 (d, 1H, $J = 6.6$ Hz, ArH), 7.37–7.61 (m, 4H, Ar′H); MS (EI), m/z (%): 479 [$M^+ - 3(CO)$] (1), 429 (5), 427 (12), 386 (14), 384 (34), 141(37), 139 (100); Anal. Found: C, 59.53; H, 6.11; N, 2.58. Calc. for $C_{28}H_{34}ClCrNO_4Si$ (564.12): C, 59.62; H, 6.08; N 2.48%.

4.4.3. exo-[η⁶-1-Triisopropylsilyl-2-methyl-4-(2′-bromobenzoyl)indoline]tricarbonylchromium(0) (18)

From **8** (158 mg, 0.37 mmol) in THF (15 ml)–TMEDA (0.5 ml), *n*-BuLi (0.66 ml, 0.93 mmol) and 2-bromobenzoyl chloride (0.2 ml, 1.52 mmol). Purification by column chromatography (petrol–ether: 90:10) and recrystallisation from ether–*n*-hexane afforded product **18**: (62 mg, 28%) as red crystals; m.p. 136–137°C; IR (cm^{-1}) ν_{max} (film): 3071 (C–H)Ar, 2951, 2870 (C–H), 1958, 1875 (C≡O), 1663 (C=O), 1589,1524, 1467 (C=C); ^{1}H-NMR: δ 1.05–1.23 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.38–1.46 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.77 (d, 1H, $J = 17.1$ Hz, CH_2), 3.47 (dd, 1H, $J = 9.0$ and 17.1 Hz, CH_2), 4.12 (m, 1H, CH), 5.06 (t, 1H, $J = 6.9$ Hz, ArH), 5.28 (d, 1H, $J = 6.9$ Hz, ArH), 5.34 (d, 1H, $J = 6.9$ Hz, ArH), 7.36–7.63 (m, 4H, Ar′H); MS (EI), m/z (%): 525 (1), 523 [$M^+ - 3(CO)$] (1), 473 (11), 471 (10), 430 (21), 428 (20), 185 (23), 183 (24), 80 (100); Anal. Found: C, 55.49; H, 5.68; N, 2.34. Calc. for $C_{28}H_{34}BrCrNO_4Si$ (608.57): C, 55.26; H, 5.63; N, 2.30%.

4.4.4. exo-(η⁶-1-Triisopropylsilyl-2-methyl-4-trimethylsilyindoline)tricarbonylchromium(0) (19)

From **8** (280 mg, 0.66 mmol) in THF(15 ml)–TMEDA (0.5 ml) *n*-BuLi (1.2 ml, 1.65 mmol) and chlorotrimethylsilane (0.5 ml, 3.73 mmol). Recrystallisation from ether–*n*-hexane afforded product **19** as yellow crystals (276 mg, 45%); m.p. 129–130°C; IR (cm^{-1}) ν_{max} (film): 2953, 2870 (C–H), 1948, 1860 (C≡O), 1537, 1522, 1500, 1445 (C=C); ^{1}H-NMR: δ 0.36 (s, 9H, $Si(CH_3)_3$), 1.06–1.24 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.37–1.44 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.46 (d, 1H, $J = 15.0$ Hz, CH_2), 3.47 (dd, 1H, $J = 9.6$ and 15.0 Hz, CH_2), 4.07 (m, 1H, CH), 4.94 (d, 1H, $J = 6.3$ Hz, ArH), 5.06 (t, 1H, $J = 6.3$ Hz, ArH), 5.19 (d, 1H, $J = 6.3$ Hz, ArH); MS (EI), m/z (%): 497 [M^+] (8), 413 (100), 361 (14), 318 (30), 73 (83); Anal. Found: C, 57.92; H, 7.95; N, 2.88. Calc. for $C_{24}H_{39}CrNO_3Si_2$ (497.75): C, 57.91; H, 7.90; N, 2.81%.

4.4.5. exo-(η₆-1-Triisopropylsilyl-2-methyl-4-triisopropylsilylindoline)tricarbonylchromium(0) (20)

From **8** (406 mg, 0.96 mmol) in THF (15 ml), *n*-BuLi (1.8 ml, 2.41 mmol) and chlorotriisopropylsilane (1.0 ml, 4.67 mmol). Purification by column chromatogra-

phy (*n*-hexane–ether: 90:10) and recrystallisation from ether–*n*-hexane afforded product **20** as yellow crystals (176 mg, 32%); m.p. 148–150°C; IR (cm^{-1}) ν_{max} (film): 2948, 2868 (C–H), 1945, 1849 (C≡O), 1521, 1495, 1464 (C=C); ^{1}H-NMR: δ 1.11–1.37 (m, 39H, Si[CH(CH$_3$)$_2$]$_3$ and CH$_3$), 1.39–1.49 (m, 6H, Si[CH(CH$_3$)$_2$]$_3$), 2.57 (d, 1H, $J = 15.9$ Hz, CH$_2$), 3.49 (dd, 1H, $J = 9.0$ and 15.9 Hz, CH$_2$), 4.02 (m, 1H, CH), 4.98 (t, 1H, $J = 6.6$ Hz, ArH), 5.10 (d, 1H, $J = 6.6$ Hz, ArH), 5.32 (d, 1H, $J = 6.6$ Hz, ArH). MS (EI), m/z (%): 581 [M$^+$] (8), 580 (11), 497 (58), 445 (84), 402 (100), 157 (30); Anal. Found: C, 61.84; H, 8.82; N, 2.44. Calc. for $C_{30}H_{51}CrNO_3Si_2$ (581.91): C, 61.92; H, 8.83; N, 2.41%.

4.5. General method for lithiation of endo-(η^6-1-triisopropylsilyl-2-methylindoline)-tricarbonylchromium(0) and electrophilic additions

n-BuLi (2.5 equivalents) was added to a solution of *endo*-(η^6-1-triisopropylsilyl-2-methylindoline)tricarbonylchromium(0) (**9**) in THF (with or without TMEDA) at −78°C and stirred for 3 h. The chosen electrophile was added, the mixture stirred for 1 h at −78°C and the solution allowed to react for 20 h at room temperature. The solution was washed with water, the aqueous layers were extracted with ether and the organic phases combined, dried, concentrated and purified by column chromatography or by preparative layer chromatography eluting with appropriate solvents system to yield compounds **21**–**27**.

4.5.1. endo-[η^6-1-Triisopropylsilyl-2-methyl-4-(2′-fluorobenzoyl)indoline]tricarbonylchromium(0) (21)

From **9** (230 mg, 0.54 mmol) in THF (15 ml)–TMEDA (0.5 ml), *n*-BuLi (1.0 ml, 1.36 mmol) and 2-fluorobenzoyl chloride (0.4 ml, 3.37 mmol). Purification by column chromatography (*n*-hexane–ether 80:20) and recrystallisation from ether–*n*-hexane afforded the product **21** as red crystals (78 mg, 26%); m.p. 124–125°C; IR (cm^{-1}) ν_{max} (film): 2950, 2878 (C–H), 1959, 1882 (C≡O), 1669 (C=O), 1613, 1519, 1456 (C=C); ^{1}H-NMR: δ 1.08–1.21 (m, 18H, Si[CH(CH$_3$)$_2$]$_3$), 1.39–1.48 (m, 6H, Si[CH(CH$_3$)$_2$]$_3$ and CH$_3$), 3.18 (d, 1H, $J = 17.4$ Hz, CH$_2$), 3.46 (dd, 1H, $J = 9.9$ and 17.4 Hz, CH$_2$), 4.06 (m, 1H, CH), 5.19 (m, 2H, ArH), 5.61 (t, 1H, $J = 3.6$ Hz, ArH), 7.12–7.60 (m, 4H, Ar′H); MS (EI), m/z (%): 547 [M$^+$] (3), 503 (3), 463 (46), 411 (18), 368 (42), 123 (100); Anal. Found: C, 61.74; H, 6.50; N, 2.49. Calc. for $C_{28}H_{34}CrFNO_4Si$ (547.67): C, 61.41; H, 6.26; N, 2.56%.

4.5.2. endo-[η^6-1-Triisopropylsilyl-2-methyl-4-(2′-chlorobenzoyl)indoline]tricarbonylchromium(0) (22)

From **9** (112 mg, 0.26 mmol) in THF (15 ml), *n*-BuLi (0.5 ml, 0.66 mmol) and 2-chlorobenzoyl chloride (0.17 ml, 1.31 mmol). Purification by column chromatography (petrol–ether: 70:30) and recrystallisation from ether–*n*-hexane afforded complex **22** as red crystals. (27 mg, 18%); m.p. 140–142°C; IR (cm^{-1}) ν_{max} (film): 2950, 2869 (C–H), 1959, 1883 (C≡O), 1669 (C=O), 1518 (C=C);^{1}H-NMR: δ 1.08–1.21 (m, 18H, Si[CH(CH$_3$)$_2$]$_3$), 1.39–1.48 (m, 6H, Si[CH(CH$_3$)$_2$]$_3$ and CH$_3$), 3.16 (d, 1H, $J = 17.4$ Hz, CH$_2$), 3.47 (dd, 1H, $J = 9.6$ and 17.4 Hz, CH$_2$), 4.06 (m, 1H, CH), 5.08 (d, 1H, $J = 6.6$ Hz, ArH), 5.14 (t, 1H, $J = 6.6$ Hz, ArH), 5.64 (d, 1H, $J = 6.6$ Hz, ArH), 7.42–7.49 (m, 4H, Ar′H); MS (EI), m/z (%): 429 (10), 427 [M$^+$ − Cr(CO)$_3$] (25), 386 (21), 384 (54), 141 (32), 139 (100); Anal. Found; C, 59.57; H, 6.37; N, 2.33. Calc. $C_{28}H_{34}ClCrNO_4Si$ (564.12): C, 59.62; H, 6.08; N 2.48%.

4.5.3. endo-[η^6-1-Triisopropylsilyl-2-methyl-4-(2′-bromobenzoyl)indoline]tricarbonylchromium(0) (23)

From **9** (182 mg, 0.43 mmol) in THF (15 ml)–TMEDA (0.5 ml), *n*-BuLi (0.8 ml, 1.09 mmol) and 2-bromobenzoyl chloride (0.4 ml, 3.05 mmol). Purification by column chromatography petrol–ether: 80:20) and recrystallisation from ether–*n*-hexane afforded complex **23** as red crystals. (39 mg, 15%); m.p. 149–151°C; IR (cm^{-1}) ν_{max} (film): 2949, 2869 (C–H), 1955, 1871 (C≡O), 1669 (C=O), 1519, 1461 (C=C). ^{1}H-NMR: δ 1.08–1.21(m, 18H, Si[CH(CH$_3$)$_2$]$_3$), 1.36–1.46 (m, 6H, Si[CH(CH$_3$)$_2$]$_3$ and CH$_3$), 3.15 (d, 1H, $J = 17.1$ Hz, CH$_2$), 3.46 (dd, 1H, $J = 9.0$ and 17.1 Hz, CH$_2$), 4.07 (m, 1H, CH), 5.07 (d, 1H, $J = 6.3$ Hz, ArH), 5.14 (t, 1H, $J = 6.3$ Hz, ArH), 5.65 (d, 1H, $J = 6.3$ Hz, ArH), 7.43–7.61(m, 4H, Ar′H); MS (EI), m/z (%): 525 (4), 523 [M$^+$ − 3CO] (6), 473 (14), 471 (15), 430 (34), 428 (37), 185 (54), 183 (56), 105 (100); Anal. Found: C, 55.54; H, 5.73; N, 2.40. Calc. for $C_{28}H_{34}BrCrNO_4Si$ (608.57): C, 55.26; H, 5.63; N 2.30%.

4.5.4. endo-(η^6-1-Triisopropylsilyl-2-methyl-4-trimethylsilylindoline)tricarbonylchromium(0) (24) and endo-(η^6-1-triisopropylsilyl-2-methyl-3-exo-trimethylsilylindoline)tricarbonylchromium(0) (25)

From **9** (456 mg, 1.07 mmol) in THF (20 ml), *n*-BuLi (2.0 ml, 2.68 mmol) and chlorotrimethylsilane (0.5 ml, 3.73 mmol). Purification by column chromatography (*n*-hexane–ether: 70:30) afforded two products as yellow solids. Following the order of elution: complex **24** (177 mg, 33%); m.p. 135–136°C; IR (cm^{-1}) ν_{max} (film): 2950, 2869 (C–H), 1944, 1855 (C≡O), 1515, 1465 (C=C). ^{1}H-NMR: δ 0.34 [s, 9H, Si(CH$_3$)$_3$], 1.06–1.19 (m, 18H, Si[CH(CH$_3$)$_2$]$_3$), 1.36–1.45 (m, 6H, Si[CH(CH$_3$)$_2$]$_3$ and CH$_3$), 2.56 (d, 1H, $J = 15.3$ Hz, CH$_2$), 3.13 (dd, 1H, $J = 9.9$ and 15.3 Hz, CH$_2$), 3.97 (m, 1H, CH), 4.92 (d, 1H, $J = 6.3$ Hz, ArH), 5.20 (t, 1H, $J = 6.3$ Hz, ArH), 5.43 (d, 1H, $J = 6.3$ Hz, ArH); MS (EI), m/z (%): 497 [M$^+$] (5), 413 (42), 361(10), 318 (14), 73 (100); Anal. Found: C, 57.70; H, 7.99; N, 2.70. Calc. for $C_{24}H_{39}CrNO_3Si_2$ (497.75): C, 57.91; H, 7.90; N, 2.81%.

Complex **25** (80 mg, 15%); m.p. 146–148°C; IR (cm^{-1}) ν_{max} (film): 2960, 2871 (C–H), 1952, 1936, 1855 (C≡O), 1532, 1456 (C=C); ^{1}H-NMR: δ 0.07 [s, 9H, $Si(CH_3)_3$], 1.08–1.22 (m, 18H, $Si[CH(CH_3)_2]_3$), 1.38–1.45 (m, 3H, $Si[CH(CH_3)_2]_3$), 1.50 (d, 1H, $J = 6.3$ Hz, CH_3), 2.07 (d, 1H, $J = 3.3$ Hz, CH), 3.97 (m, 1H, CH), 4.83 (t, 1H, $J = 6.0$ Hz, ArH), 5.18 (d, 1H, $J = 6.0$ Hz, ArH), 5.28 (t, 1H, $J = 6.0$ Hz, ArH), 5.46 (d, 1H, $J = 6.0$ Hz, ArH); MS (EI), m/z (%): 441 [$M^+ - 2(CO)$] (2), 413 (29), 361 (24), 318 (3), 73 (100); HRMS (EI) Found: 497.1872. Calc. for $C_{24}H_{39}CrNO_3Si_2$: 497.1874.

4.5.5. endo-(η^6-1-Triisopropylsilyl-2-methyl-4-triisopropylindoline)tricarbonylchromium(0) (**26**) and endo-(η^6-1-triisopropylsilyl-2-methyl-3-exo-triisopropylsilylindoline)tricarbonylchromium(0) (**27**)

From **9** (134 mg, 0.32 mmol) in THF (15 ml), *n*-BuLi (0.43 ml, 0.63 mmol) and chlorotriisopropylsilane (0.25 ml, 1.17 mmol). After purification by preparative layer chromatography (*n*-hexane–dichloromethane: 75:25) afforded products **26** as yellow crystals (after recrystallisation from ether–*n*-hexane) and complex **27** as a yellow oil. Following the order of elution: complex **26** (26 mg, 14%); m.p. 126–128°C; IR (cm^{-1}) ν_{max} (film): 2948, 2869 (C–H), 1950, 1866 (CO), 1514, 1459 (C=C); ^{1}H-NMR: δ 1.04–1.21(m, 36H, $Si[CH(CH_3)_2]_3$), 1.32–1.39 (m, 6H, $Si[CH(CH_3)_2]_3$), 1.43 (d, 3H, $J = 6.6$ Hz, CH_3), 2.56 (d, 1H, $J = 15.3$ Hz, CH_2), 3.17 (dd, 1H, $J = 9.9$ and 15.3 Hz, CH_2), 3.91 (m, 1H, CH), 5.07 (d, 1H, $J = 6.6$ Hz, ArH), 5.17 (t, 1H, $J = 6.6$ Hz, ArH), 5.57 (d, 1H, $J = 6.6$ Hz, ArH); MS (EI), m/z (%): 581 [M^+] (6), 580 (11), 497 (41), 445 (22), 402 (17), 157 (9), 59 (100); Anal. Found: C, 62.03; H, 8.98; N, 2.46. Calc. for $C_{30}H_{51}CrNO_3Si_2$ (581.91): C, 61.92; H, 8.83; N, 2.41%. Complex **27** (6 mg, 3%); IR (cm^{-1}) ν_{max} (film): 2948, 2868 (C–H),1953, 1854, 1831 (C≡O), 1528, 1457 (C=C); ^{1}H-NMR: δ 1.06–1.23 (m, 36H, $Si[CH(CH_3)_2]_3$), 1.41–1.46 (m, 6H, $Si[CH(CH_3)_2]_3$), 1.58 (d, 3H, $J = 6.3$ Hz, CH_3), 2.48 (d, 1H, $J = 3.3$ Hz, CH), 4.12 (m, 1H, CH), 4.81 (t, 1H, $J = 6.3$ Hz, ArH), 5.21 (d, 1H, $J = 6.3$ Hz, ArH), 5.30 (t, 1H, $J = 6.3$ Hz, ArH), 5.53 (d, 1H, $J = 6.3$ Hz, ArH); MS (EI), m/z (%): 581 [M^+] (3), 580 (3), 497 (16), 445 (4), 402 (1), 157 (5), 59 (100); HRMS (EI) Found: 581.2822. Calc. for $C_{30}H_{51}CrNO_3Si_2$: 581.2813.

4.6. General procedure for the decomplexation of some indoline complexes

A solution of complexes (**12**, **19** and **20**) in ether or chloroform was exposed to air and sunlight at room temperature until TLC indicated that the reaction had gone to completion. Filtration through silica and removal of the solvent gave decomplexed indolines which were further purified by preparative layer chromatography (*n*-hexane–ether: 70:30) to afford products **28**–**30**.

4.6.1. 1,2-Dimethyl-4-(2′-chlorobenzoyl)indoline (**28**)

Complex **12** (13 mg, 0.030 mmol) in chloroform afforded indoline **28** as a yellow oil (6 mg, 68%); IR (cm^{-1}) ν_{max} (film): 3065 (CH)Ar, 2960, 2924, 2853 (C–H), 1665 (C=O), 1590, 1467 (C=C); ^{1}H-NMR: δ 1.35 (d, 3H, $J = 5.7$ Hz, CH_3), 2.76 (s, 3H, NCH_3), 2.84 (d, 1H, $J = 7.8$ Hz, CH_2), 3.48–3.58 (m, 2H, CH_2 and CH), 6.59 (d, 1H, $J = 7.8$ Hz, ArH), 6.72 (d, 1H, $J = 7.8$ Hz, ArH), 7.09 (t, 1H, $J = 7.8$ Hz, ArH), 7.34–7.43 (m, 4H, Ar′H); MS (EI), m/z (%): 287 (8), 285 [M^+] (23), 272 (4), 270 (13), 141(33), 139(100); HRMS (EI) Found: 285.0923. Calc. for $C_{17}11_{16}C1N0$: 285.0920.

4.6.2. 1-Triisopropylsilyl-2-methyl-4-trimethylsilylindoline (**29**)

Complex **19** (85 mg, 0.170 mmol) in ether afforded indoline **29** as a colourless oil (34.1 mg, 59%); IR (cm^{-1}) ν_{max} (film): 3051 (C–H)Ar, 2954, 2894, 2867 (C–H), 1666 (C=O), 1569, 1466 (C=C); ^{1}H-NMR: δ 0.27 (s, 9H, $Si(CH_3)_3$), 1.06–1.18 (m, 21H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.34–1.42 (m, 3H, $Si[CH(CH_3)_2]_3$), 2.59 (d, 1H, $J = 15.0$ Hz, CH_2), 3.19 (dd, 1H, $J = 8.7$ and 15.0 Hz, CH_2), 3.97 (m, 1H, CH), 6.71 (d, 1H, $J = 7.5$ Hz, ArH), 6.78 (d, 1H, $J = 7.5$ Hz, ArH), 6.96 (t, 1H, $J = 7.5$ Hz, ArH); MS (EI), m/z (%): 361 [M^+] (35), 346 (8), 318 (64), 73 (100); HRMS (EI) Found: 361.2603. Calc. for $C_{21}H_{39}NSi_2$: 361.2621.

4.6.3. 1-Triisopropylsilyl-2-methyl-4-triisopropylsilylindoline (**30**)

Complex **20** (16 mg, 0.027 mmol) in ether afforded indoline **30** as a colourless oil (8 mg, 63%); IR (cm^{-1}) ν_{max} (film): 3054 δ(C–H)Ar, 2945, 2866 (C–H), 1567, 1465 (C=C); ^{1}H-NMR: δ 1.04–1.28 (m, 39H, $Si[CH(CH_3)_2]_3$ and CH_3), 1.33–1.46 (m, 6H, $Si[CH(CH_3)_2]_3$), 2.62 (d, 1H, $J = 15.0$ Hz, CH_2), 3.17 (dd, 1H, $J = 7.2$ and 15.0 Hz, CH_2), 3.92 (m, 1H, CH), 6.71 (d, 1H, $J = 7.5$ Hz, ArH), 6.80 (d, 1H, $J = 7.5$ Hz, ArH), 6.94 (t, 1H, $J = 7.5$ Hz, ArH); MS (EI), m/z (%): 445 [M^+] (24), 430 (2), 402 (19), 59 (100); HRMS (EI) Found: 445.3537. Calc. for $C_{27}H_{51}NSi_2$: 445.3560.

5. Unlinked reference

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