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Peri-Directed 7-Substitution in η^6-Indoletricarbonylchromium(0) Complexes

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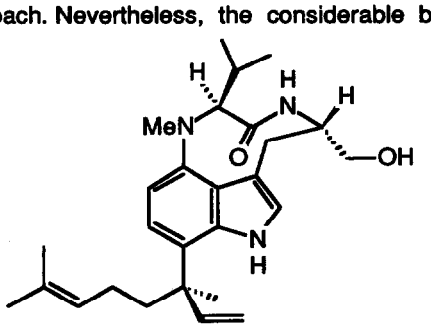
Abstract: 7-Substituted indoles were prepared by the lithiation – electrophilic quenching of 1-methyl-, 1-methoxymethyl-, and 1-(2-trimethylsilylethoxymethyl)indoletricarbonylchromium(0) complexes. C-2 of the 1-methylindole series had to be blocked to achieve subsequent 7- (and 4-) metallation, but the other series could be directly metallated at C-7 without attack at C-4 by 1-alkoxymethyl directed lithiation. Metallation at C-2 in the 1-alkoxymethyl series was avoided by the use of the 2-trimethylsilyl or the 3-methyl analogues. No conditions were found to effect the removal of the methoxymethyl group, but the 2-trimethylsilylethoxymethyl group was efficiently cleaved with 'anhydrous' tetrabutylammonium fluoride.

The dearth of general methods for the direct functionalisation of indoles in the carbocyclic ring[1] results in this being an underdeveloped strategy, despite the inherent directness of such an approach. Nevertheless, the considerable biological activity of some natural indoles, such as



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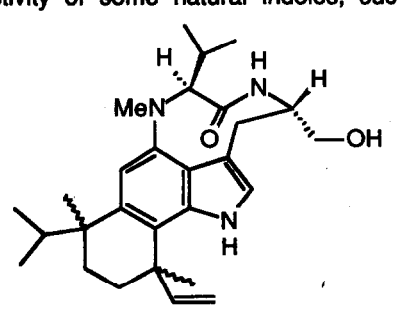

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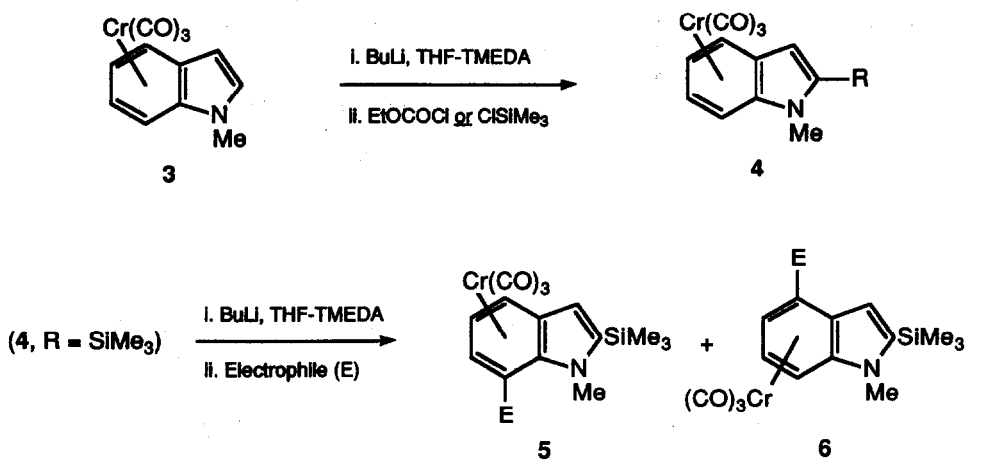
lyngbyatoxin A (1)[2] and teleocidins B-1 to B-4 (2)[3], provides a strong stimulus to create such chemistry and so develop the strategy. We have previously shown how, by means of appropriate

blocking agents on the indolic nitrogen atom, indoletricarbonylchromium(0) complexes allow the direct functionalisation at C-4 of the indole nucleus *via* a lithiation / electrophilic quench sequence[4]. We now extend this chromium mediated functionalisation to 7-substitution[5].

The well documented electron withdrawing effect of an appended tricarbonylchromium group on an aromatic ring[6] renders the ring susceptible to both nucleophilic addition and deprotonation. Kozikowski *et al* have used the former process in their investigation of the nucleophilic attack of carbanions on *N*-protected indole complexes[7], a process which occurs at C-4 or C-7 depending on the carbanion. However this approach requires mild oxidation to generate the substituted indole from the initial addition complex and the oxidation results in the loss of the chromium group.

We chose to examine the deprotonation of indoletricarbonylchromium(0) complexes as a means to achieve substitution in a manner which avoids the loss of the tricarbonylchromium group, and thus gives scope for additional chromium-directed regio- and stereocontrol.

Treatment of the *N*-methyl complex (3) with butyl lithium in tetrahydrofuran (THF) and *N,N,N'N'*-tetramethylethylenediamine (TMEDA) followed by reaction with ethyl chloroformate gave 2-ethoxycarbonyl-1-methylindole complex (4, R = CO_2Et) in 78% yield (Scheme 1). The absence of TMEDA depressed the yield to 27% and unreacted (3) was recovered. Quenching the lithio- species with chlorotrimethylsilane gave a product (4, R = $SiMe_3$; 60%) which on decomplexation was identical in all respects with 1-methyl-2-trimethylsilylindole obtained by a literature route[8b]. Uncomplexed *N*-protected-indoles are also deprotonated at C-2[8] but this requires higher temperatures (–10°C to +30°C) and under the above conditions 1-methylindole was unaffected.



Scheme 1

In order to establish the second site of deprotonation the 2-trimethylsilyl complex (4, R = $SiMe_3$), generated *in situ*, was treated with a further equivalent of butyl lithium as above and quenched with ethyl chloroformate. This gave, by high resolution NMR spectroscopic analysis, a > 4:1 ratio of the 7-substituted indole (5, R = CO_2Et; 67% after chromatography) and the 4-

substituted indole (6, R = CO_2Et) complexes. Although the NMR spectrum of decomplexed (5, R = CO_2Et) showed a clear ABC splitting pattern between δ 7.1–7.7 and the chemical shift of the *N*-methyl group (δ 4.24) suggested 7-substitution, the distinction was fully resolved by an X-ray analysis[9] which showed our interpretation to be correct.

With the structure of (5) established the lithiated complex was treated with a series of electrophiles to give the substituted indole complexes (Table 1). In each case (except Run 2) the 7-substituted isomer was isolated pure by column chromatography, but the 4-substituted isomer could never be completely separated from the mixture. Similarly, the ratio of products remained approximately constant which suggests that there is no equilibration of the lithiated species[10] during electrophilic quenching and that the ratio is that of kinetic deprotonation at the two sites.

The products were readily decomplexed[11] to generate the parent indoles in excellent yield. Aromatic desilylation using 33% aqueous trifluoroacetic acid[12] at room temperature converted 1-methyl-2-trimethylsilylindole into 1-methylindole in 79% yield in 2.5 h. Desilylation of 7-ethoxycarbonyl-1-methyl-2-trimethylsilylindole required a more acidic medium (67% aqueous trifluoroacetic acid), which depressed the yield of product to 53%.

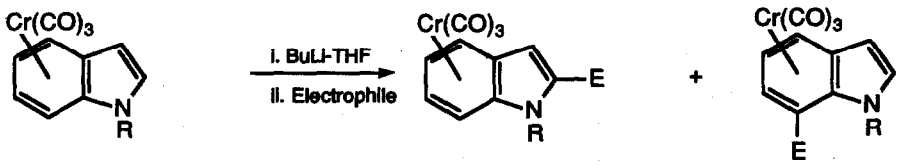
Table 1: Synthesis of 7-Substituted-1-methyl-2-trimethylsilylindoles

		Indole complexes (5) / (6)			Free indole	
Run	Electrophile	Yield[a]	(b)	m.p.(°C)[a]	Yield[c](%)	m.p.(°C)
1	$ClCO_2Et$	67	(85)	107	78	oil
2	MeI	—[d]	(64)	117–9[e]	—	109–110
3	PhCHO	63	(83)	148 (dec)	89	110
4	CH_2=CHCHO	60	(74)	155 (dec)	92	oil
5	PhSCl	51	(73)	135–140 (dec)	80	102–104
6	Me_2C=$CHCH_2Br$	43	(61)	119–119.5	77	106.5–107

[a] of (5) after chromatography.
[b] total of mixed isomers, (5) + (6).
[c] of decomplexation.
[d] the 4 / 7 isomer mixture was inseparable.
[e] of mixed isomers

As the lithiation of (3) was not fully regioselective, and the overall yield of 7-substituted indoles was thereby diminished, we turned to the methoxymethyl group for *N*-protection on the basis that the chelating properties of this group[13] would direct the formation of a 7-lithio species in the second lithiation step. In the event, the lithiation of 1-methoxymethylindole complex (7, R = CH_2OMe) with a slight excess of butyl lithium and a quench with chlorotrimethylsilane produced (Scheme 2) not just the expected 2-trimethylsilyl compound (8, R = CH_2OMe, E = $SiMe_3$) but, as the major product, the 7-trimethylsilyl complex (9, R = CH_2OMe, E = $SiMe_3$). The site of

substitution was confirmed by the nOe difference spectra of the decomplexed indole. The complexes (8, R = CH_2OMe, E = $SiMe_3$) and (9, R = CH_2OMe, E = $SiMe_3$) were present in a ratio of approximately 1 : 4, together with some 2,7-di-trimethylsilyl compound.



7 8 9

Scheme 2

The subsequent use of an exact equivalent of butyl lithium maximised the formation of monosilylated complexes and the lithiation was performed under a range of conditions to try to improve the ratio of C-7 to C-2 substitution. Though the ratio was found to be temperature dependent the effect is not marked and some 2-substitution was always evident. TMEDA was found to be unnecessary, though not significantly deleterious. Lithiation under optimum conditions and careful crystallisation of the product mixture gave a 66% yield of 1-methoxymethyl-7-trimethylsilylindole complex (9, R = CH_2OMe, E = $SiMe_3$). In an analogous manner, 3,3-dimethylallyl bromide gave a 49% yield of the 7-substituted complex which was decomplexed photochemically[11] to the parent indole in 93% yield.

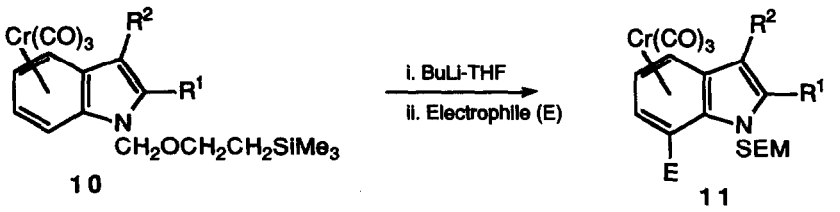
Attempts at extending this strategy to unprotected indoles by removal of the methoxymethyl group[14] met with failure. Under both protic and Lewis acidic conditions, 1-methoxymethylindole polymerised to give undetermined products, while the action of a powerful soft nucleophile[15] (LiSMe in HMPA) on the complexed indole only resulted in decomplexation.

We required a protecting group for indole which would retain the complexing ability of the methoxymethyl group yet be removable. The 2-trimethylsilylethoxymethyl (SEM) group has already been used for directing lithiation to the 2-position of pyrrole and indole[16] and is removable with 'anhydrous' tetrabutylammonium fluoride.

Lithiation of 1-(2-trimethylsilylethoxymethyl)indole complex (7, R = SEM) under similar conditions to those used for 1-methoxymethyl indole complex, followed by reaction with chlorotrimethylsilane, did produce a mixture of the 2- and 7-substituted complexes (8, R = SEM, E = $SiMe_3$) and (9, R = SEM, E = $SiMe_3$) (Scheme 2). The reaction showed little temperature dependence of the site of lithiation in the range –40°C to –100°C and resulted in a ratio of C-7 : C-2 lithiation of ≤1:1. The products were inseparable, the ratio being determined by comparison of the ^1H NMR spectrum of the mixture with that of pure 2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole complex (*vide infra*).

We returned to the idea of blocking the 2-position with a trimethylsilyl group as used in the 1-methyl series. The method of Katritsky *et al*,[17] with carbon dioxide as a temporary *N*-protection during lithiation, (7, R = H) cleanly gave the 2-trimethylsilylated indole complex (8, R = H, E =

$SiMe_3$) in 83% yield. It is notable that the temporary protectant (CO_2) was removed more readily in the complexed series here than in the uncomplexed. Efforts to extend this methodology to 7-substitution by repeating the process led either to recovery of starting material (with n-BuLi, –78°C and –30°C) or decomposition (t-BuLi, –78°C and –30°C). The 2-silylated complex was therefore protected with the 2-trimethylsilylethoxymethyl group to give (**10**, R^1 = $SiMe_3$, R^2 = H; 77%) and lithiation of this and reaction with electrophiles as before (Scheme 3) cleanly gave the 7-substituted isomers (**11**, R^1 = $SiMe_3$, R^2 = H) in good yield (Table 2, Runs 1–3)



Scheme 3

Table 2: Lithiation of 1-(2-Trimethylsilylethoxymethyl)indole Complexes (**10**)

Run	Substrate(10) R_1	R_2	Electrophile	Yield of (11) (%)	Coreagents
1	TMS	H	MeI	95	
2	TMS	H	DMF	70	
3	TMS	H	allyl bromide	69	CuBr.SMe_2
4	H	Me	TMSCl	88	
5	H	Me	EtOCOCl	66	
6	H	Me	$(CH_3)_3SnCl$	65	
7	H	Me	allyl bromide	69	CuBr.SMe_2
8	H	Me	2-Bromo-2-butene	68	CuBr.SMe_2+$Pd(PPh_3)_4$

We then looked at the influence of a substituent at C-3 on the balance between lithiation at C-2 and at C-7. Lithiation of the 3-methyl indole complex (**10**, R^1 = H, R^2 = Me) and quench with chlorotrimethylsilane (Table 2, Runs 4–8) gave a single product which was solely the product of reaction at C-7 as determined by high field NMR spectroscopy. Thus the steric influence of a 3-methyl group is sufficient to completely bias the reaction towards 7-substitution. Other simple electrophiles reacted similarly with appropriate modification of the reaction conditions. When the 7-trimethylsilyl compound (**11**, R^1 = H, R^2 = Me, E = $SiMe_3$) was further lithiated and quenched as before, the 2,7-di(trimethylsilyl)indole complex was formed in high yield (82%). Further lithiation gave a complex mixture which was not investigated further.

In a control experiment, the uncomplexed 3-methyl-1-(2-trimethylsilylethoxymethyl)indole was lithiated in dry dimethoxyethane at –23°C and trimethylsilylated as previously described[16], to give the 2-substituted product (35%) together with unchanged starting material (40%). In particular, no product of 7-substitution was detectable.

Finally, the removal of the 2-trimethylsilylethoxymethyl group was carried out as described before on (7, R = SEM) (62%), (11, R^1 = E = H, R^2 = Me) (71%) and (11, R^1 = H, R^2 = Me, E = $C(CH_3)=CHCH_3$) (55%).

This deprotection procedure completed the 7-functionalisation of the indoles. This combination of tricarbonylchromium activation and *peri*-ligand regiodirected metallation allows the introduction of a range of 7-substituents into 2-(trimethylsilyl)-blocked or 3-substituted indoles in a regiospecific process of good synthetic potential, and is the subject of further exploitation in our laboratories.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Melting points were carried out on a Kofler hot stage and are uncorrected; infrared spectra were recorded on Perkin Elmer 1700 FT spectrometer; ^1H NMR on a Perkin Elmer R32 (90 MHz), Bruker WH–250 FT (250 MHz), or Jeol GSX FT (270 MHz) spectrometers, the latter with a GSX data system. Gas chromatograms were recorded on Varian Vista 6000 chromatograph with a chromosorb WHP 80–100 mesh column (OV 101), with a Varian Vista CDS 401 data system.

All reactions involving complexes or butyl lithium were carried out under an atmosphere of dry, oxygen free nitrogen. Unless otherwise stated, petrol refers to petroleum ether b.p. 60–80°C.

General procedure for complexation:— A mixture of the indole (1.1 equiv.) and hexacarbonylchromium (1.0 equiv.) in deoxygenated di-n-butyl ether–THF (10 : 1)[18] were heated under reflux for 12–40 h. using a simplifiedStröhmeier apparatus[19]. The resulting orange solution was cooled, filtered through Celite with ether, and concentrated under reduced pressure. Flash chromatography or dry flash chromatography and / or recrystallisation (petrol–ether or petrol–dichloromethane) as appropriate gave the indole complexes.

In addition to compounds previously described in full, so prepared were:—

η^6-*(1-Methylindole)tricarbonylchromium(0)* (3). — Complexation of 1-methyl-indole (2.16 g, 16.5 mmol) with hexacarbonylchromium (3.36 g, 15 mmol) gave the complex (3) (3.54 g, 88%) as yellow needles, m.p. 131–132°C (dec.) (from ether–THF–petrol); ν_{max} ($CHCl_3$) 1955, 1865, 1555, 1455, 1300, 1130 and 630 cm^{-1}; δ_H ($CDCl_3$) 3.65 (3H, s, N-*Me*), 5.05 (1H, t, *J* 6 Hz, 5/6-*H*), 5.35 (1H, t, *J* 6 Hz, 6/5-*H*), 6.0 (1H, d, *J* 6 Hz, 4-*H*), 6.2–6.4 (2H, m, 3-*H* and 7-*H*) and 7.05 (1H, d, *J* 6 Hz, 2-*H*); *m/z* 267 (M^+), 211, 183 and 131 (100%). (Found: C, 54.07; H, 3.35; N, 5.26. $C_{12}H_9CrNO_3$ requires C, 53.94; H, 3.39; N, 5.24%).

η^6-*(1-Methoxymethylindole)tricarbonylchromium(0)* (7, R = CH_2OMe)— Complexation of 1-methoxymethylindole (403 mg, 2.5 mmol), prepared by Sundberg's method[13], afforded the *complex* (7, R = CH_2OMe) (610 mg, 90%) as yellow prisms, m.p. 153–5°C (dec.) (from THF–ether–petrol) which were insoluble in the common NMR solvents; ν_{max} ($CHCl_3$) 1955, 1870,

1440, 1295, 1120, 1095, 660 and 625 cm^{-1}; *m/z* 297 (*M*+), 266, 241, 213, 183, 161 and 130 (100%). (Found: C, 52.63; H, 3.69; N, 4.74. $C_{13}H_{11}CrNO_4$ requires C, 52.53; H, 3.73; N, 4.71%).

η^6-*(3-Methylindole)tricarbonylchromium(0)*— Complexation of 3-methyl-indole (1.97 g, 1.1 eq) with hexacarbonylchromium(0) (3 g, 13.6 mmol) under the described conditions followed by trituration with petrol–ether gave the *title complex* as yellow crystals (2.87 g, 79%) no sharp m.p., darkens markedly above 110°C; δ_H (270 MHz, $CDCl_3$) 2.25 (3H, s, *Me*), 5.1 (1H, t, *J* 6.8 Hz, 6-*H*), 5.4 (1H, t, *J* 6.8 Hz, 5-*H*), 6.1 (1H, d, *J* 6.8 Hz, 7-*H*), 6.30 (1H, d, *J* 6.8 Hz, 4-*H*) and 6.95 (1H, s, 2-*H*); *m/z* 267 (*M*+), 211, 183 and 130. (Found: C, 53.86; H, 3.31; N, 5.27. $C_{12}H_9CrNO_3$ requires C, 53.94; H, 3.39; N, 5.24%).

General Procedure for the lithiation of N*-protected indole complexes*: *Procedure A*— Butyl lithium (1.1 eq) was added dropwise to a solution of the indole complex in dry THF at –78°C. After 1 h at this temperature, excess electrophile was added and allowed to react for 30 min before the solution was allowed to warm to room temperature.

Procedure B— Butyl lithium (1.0 eq.) was added to a solution of the complex in THF–TMEDA (30 : 1) at –78°C. After 1h at –78°C, excess electrophile was added and allowed to react at this temperature for 1 h before the solution was allowed to warm to room temperature.

Procedure C— As for procedure B but the reaction was quenched with chlorotrimethylsilane (1.0 eq) then lithiated once more *in situ* by procedure B.

Preparation of 2-substituted-1-methylindole complexes— Procedure B, followed by acidic work up and purification by column chromatography on silica gel.

So prepared were:—

η^6-*(2-Ethoxycarbonyl-1-methylindole)tricarbonylchromium(0)* (4, R = CO_2Et) — Eluant petrol–ether (1 : 1), crystallised from petrol–ether or petrol–diisopropyl ether to give the *complex* (4, R = CO_2Et) (530 mg, 78%) m.p. 124°C; ν_{max} ($CDCl_3$) 1960, 1885, 1710 and 1145 cm^{-1}; δ_H ($CDCl_3$) 1.4 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 3.9 (3H, s, N-*Me*), 4.35 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 5.15 (1H, t, *J* 7 Hz, 5-*H*), 5.55 (1H, d, *J* 7 Hz, 6-*H*), 6.0 (1H, d, *J* 7 Hz, 4-*H*), 6.35 (1H, d, *J* 7 Hz, 7-*H*) and 7.2 (1H, s, 3-*H*); *m/z* 339 (*M*+), 255 (100%) and 203. (Found: C, 52.89; H, 3.89; N, 4.06. $C_{15}H_{13}CrNO_5$ requires C, 53.10; H, 3.86; N, 4.13%).

Decomplexation of (4, R = CO_2Et) (530 mg, 1.56 mmol) in acetonitrile gave 2-ethoxycarbonyl-1-methylindole (295 mg, 93%) as a clear oil which solidified on standing. Preparative t.l.c. followed by precipitation from petrol at –78°C gave analytically pure material as white crystals , m.p. 61–61.5°C; $\nu_{max.}$ ($CDCl_3$) 2980, 1705, 1520, 1400, 1245, 1230, 1170, 1150, 1135 and 1085 cm^{-1}; δ_H ($CDCl_3$) 1.4 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 4.05 (3H, s, N-*Me*), 4.4 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$) and 7.0–7.8 (5H, m, 3,4,5,6,7-*H*); *m/z* 203 (*M*+, 100%), 188, 175 and 158. (Found: C, 70.70; H, 6.45; N, 6.75. $C_{12}H_{13}NO_2$ requires C, 70.92; H, 6.45; N, 6.89%).

η^6-*(1-Methyl-2-trimethylsilylindole)tricarbonylchromium(0)* (4, R = $SiMe_3$) — Eluant petrol–ether (80 : 20); orange oil (563 mg, 83%), crystallised from petrol–ether to give (4, R = $SiMe_3$) (410 mg, 60%) as bright orange prisms, m.p. 105°C; ν_{max} ($CDCl_3$) 1950, 1860, 1455, 1255, 1210, 1120, 1070, 835 and 625 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, $SiMe_3$), 3.7 (3H, s, N-*Me*), 5.0 (1H, t, *J* 6 Hz, 5-*H*), 5.45 (1H, d, *J* 6 Hz, 6-*H*), 5.95 (1H, d, *J* 6 Hz, 4-*H*), 6.35 (1H, d, *J* 6 Hz, 7-*H*) and 6.5 (1H, s, 3-*H*); *m/z* 339 (*M*+), 269, 255 (100%), 203 and 188. (Found: C, 53.33; H, 5.02; N, 4.13. $C_{15}H_{17}CrNO_3Si$ requires C, 53.08; H, 5.05; N, 5.13%).

Decomplexation of (4, R = $SiMe_3$) (264 mg, 0.78 mmol) in acetonitrile gave 1-methyl-2-trimethylsilylindole (150 mg, 95%) as a clear oil identical to an authentic sample prepared by a

literature method

General Procedure for the preparation of 7-substituted-1-methyl-2-trimethylsilylindole complexes— As procedure C above, with dilute hydrochloric acid work up, ether extraction, followed by chromatography. So prepared were:—

η^6-*(7-Ethoxycarbonyl-1-methyl-2-trimethylsilylindole)tricarbonyl-chromium(0)* (5, E = CO_2Et) — Gradient elution with petrol–ether (100 : 0 → 85 : 15) and crystallisation from petrol gave the *complex* (5, E = CO_2Et) (825 mg, 67%) as red crystals. Recrystallisation from diisopropyl ether–petrol gave analytically pure, X-ray crystallographic material as red needles, m.p. 107°C; ν_{max} ($CDCl_3$) 1960, 1885, 1710, 1245, 1190, 1130, 1100, 835 and 615 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 1.45 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 3.85 (3H, s, N-*Me*), 4.45 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 4.95 (1H, t, *J* 6 Hz, 5-*H*), 6.05 (1H, d, *J* 6 Hz, 4-*H*), 6.5 (1H, d, *J* 6 Hz, 6-*H*) and 6.55 (1H, s, 3-*H*); *m/z* 411 (*M*$^+$), 355, 327 (100%), 312, 275, 255, 230 and 214. (Found: C, 52.76; H, 5.16; N,3.42. $C_{18}H_{21}CrNO_5Si$ requires C, 52.54; H, 5.14; N,3.40%).

Decomplexation of the above complex (800 mg, 1.95 mmol) gave 7-ethoxycarbonyl-1-methyl-2-trimethylsilylindole (482 mg, 90%) as a clear oil, preparative t.l.c. of which gave analytically pure material; ν_{max} ($CHCl_3$) 2950, 1700, 1440, 1360, 1340, 1300, 1200, 1100, 1070, 875 and 680 cm^{-1}; δ_H ($CDCl_3$) 0.4 (9H, s, $SiMe_3$), 1.4 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 3.9 (3H, s, N-*Me*), 4.4 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 6.75 (1H, s, 3-*H*), 7.05 (1H, t, *J* 7 Hz, 5-*H*) and 7.5–7.8 (2H, m, 4,6-*H*); *m/z* 275 (*M*$^+$, 100%), 260, 230 and 214. (Found: C, 65.48; H, 7.77; N, 5.05. $C_{15}H_{21}NO_2Si$ requires C, 65.41; H, 7.68; N, 5.09%).

1,7-Dimethyl-2-trimethylsilylindole (5, E = Me)— Excess methyl iodide (3.0 g) as electrophile. Work-up as above gave an inseparable mixture of 7- and 4- methylated products (5, 6, E = Me) in the ratio of *ca.* 5 : 1 (by ^1H NMR analysis).

Decomplexation of this mixture gave (5, E = Me) as fine white needles, m.p. 109–110°C (from petrol at –78°C), preparative t.l.c. of which afforded analytically pure material; ν_{max} ($CHCl_3$) 2950, 1450, 1305, 1110, 865, 835 and 660 cm^{-1}; δ_H ($CDCl_3$) 0.4 (9H, s, Si*Me*$_3$), 2.75 (3H, s, 7-*Me*), 4.1 (3H, s, N-*Me*), 6.6 (1H, s, 3-*H*) and 6.8–7.5 (3H, m, 4,5,6-*H*); *m/z* 217(*M*$^+$) and 202 (100%). (Found: C, 71.74; H, 8.85; N, 6.40. $C_{13}H_{19}NSi$ requires C, 71.83; H, 6.81; N, 6.44%).

η^6-*[1-Methyl-7-(α–hydroxybenzyl)-2-trimethylsilylindole]tricarbonylchromium(0)* [5, E = CH(OH)Ph]— Gradient elution with petrol–ether (85 : 15 → 70 : 30) gave the *complex* [5, E = CH(OH)Ph] (840 mg, 63%) as a diastereomeric mixture, orange prisms, m.p. 149°C (dec.) (from petrol / ether); ν_{max} ($CDCl_3$) 3580, 1950, 1860, 1445, 1240, 1100, 1065, 830 and 620 cm^{-1}; δ_H ($CDCl_3$) 0.4 (9H, s, Si*Me*$_3$), 3.55 and 3.75 (1H, d, *J* 4 Hz, exch., O*H*) 3.8 and 4.1 (3H, s, N-*Me*), 4.8–5.8 (2H, m, 5,6-*H*) 6.2–6.7 (3H, m, part exch., 3,4-*H* and C*H*OHPh) and 7.2–7.6 (5H, m, *Ph*); *m/z* 445 (*M*$^+$), 429, 361, 345, 309 and 293 (100%). (Found: C, 59.22; H, 5.17; N, 3.14. $C_{22}H_{23}CrNO_4Si$ requires C, 59.31; H, 5.20; N 3.14%).

Decomplexation of this complex (300 mg, 0.67 mmol) gave *1-methyl-7-(α-hydroxybenzyl)-2-trimethylsilylindole* (185 mg, 89%) as white crystals m.p. 110°C (from petrol at –78°C). Preparative t.l.c., eluant: petrol (b.p. 30–40°C)–ether (90 : 10) gave pure material; ν_{max} ($CDCl_3$) 3600, 2960, 1445, 1310, 1250, 1075, 810 and 645 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 2.6 (1H, d, *J* 5 Hz, O*H*), 3.9 (3H, s, N-*Me*), 6.4 (1H, d, *J* 5 Hz, C*H*OHPh), 6.65 (1H, s, 3-*H*) and 6.8–7.6 (8H, m, 4,5-*H* and *Ph*); *m/z* 309 (*M*$^+$, 100%) and 292. (Found: C, 73.50; H, 7.53; N, 4.37. $C_{19}H_{23}NOSi$ requires C, 73.74; H, 7.49; N, 4.53%).

η^6-*[7-(1'-Hydroxyprop-2'-enyl)-1-methyl-2-trimethylsilylindole]tricarbonylchromium(0)* {5, E =

CH(OH)CH=CH_2}— Gradient elution with petrol–ether (85 : 15 → 60 : 40), followed by crystallisation from petrol gave the *complex* {5, E = CH(OH)CH=CH_2} (710 mg, 60%) as orange crystals, m.p. 155°C (dec.) (from petrol–ether).; ν_{max} ($CDCl_3$) 3580, 2970, 1950, 1860, 1445, 1405, 1380, 1295, 1250, 1100, 1070, 980, 830 and 620 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 2.2–2.3 (1H, m, exch., O*H*), 3.85 and 4.05 (3H, s, N-*Me*), 4.8–6.5 (7H, m, 4,5,6-*H* and C*H*OHC*H*=CH_2) and 6.45 (1H, s, 3-*H*); *m/z* 395 (M^+), 389, 339, 323, 311 (100%), 295, 259 and 243. (Found: C, 54.50; H, 5.29; N, 3.52. $C_{18}H_{21}CrNO_4Si$ requires C, 54.67; H, 5.35; N, 3.54%).

Decomplexation of the above complex gave *7-(1'-hydroxyprop-2'-enyl)-1-methyl-2-trimethylsilylindole* (120 mg, 92%) as a clear unstable oil which gave analytically pure material after preparative t.l.c.; ν_{max} ($CDCl_3$) 3590, 2960, 1445, 1400, 1300, 1060, 980, 810 and 660 cm^{-1}; δ_H ($CDCl_3$) 0.4 (9H, s, Si*Me*$_3$), 2.05 (1H, d, *J* 6 Hz, O*H*), 4.15 (3H, s, N-*Me*), 5.2–7.6 (7H, m, 4,5,6-*H* and C*H*OHC*H*=CH_2) and 6.65 (1H, s, 3-*H*); *m/z* 259 (M^+). (Found: C, 69.76; H, 8.35; N, 5.24. $C_{15}H_{21}NOSi$ requires C, 69.45; H, 8.16; N, 5.40%).

η^6-*(1-Methyl-7-phenylthio-2-trimethylsilylindole)tricarbonylchromium(0)* (5, E = SPh) — Eluant: petrol–ether (90 : 10) gave the *complex* (5, E = SPh) (680 mg, 51%) as golden crystals, m.p. 135–140°C (dec.) (from petrol–ether); ν_{max} ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 4.0 (3H, s, N-*Me*), 5.05 (1H, m, 5-*H*), 5.5 (1H, m, 6-*H*), 6.4 (1H, m, 4-*H*), 6.5 (1H, s, 3-*H*) and 7.1–7.4 (5H, br.s, *Ph*); *m/z* 447 (M^+), 363 and 311 (100%). (Found: C, 56.27; H, 4.65; N, 3.08; S, 7.50. $C_{21}H_{21}CrNO_3SSi$ requires C, 56.36; H, 4.73; N, 3.13; S, 7.16%).

Decomplexation of the above complex (320 mg, 0.72 mmol) gave *1-methyl-7-phenylthio-2-trimethylsilylindole* (190 mg, 85%) as a clear oil which was crystallised from petrol at –78°C to give colourless crystals, m.p. 104.5–106°C; ν_{max} ($CDCl_3$) 3060, 2950, 1580, 1440, 1305, 1105, 1070, 830, 805 and 635 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 4.1 (3H, s, N-*Me*), 6.7 (1H, s, 3-*H*) and 6.8–7.8 (8H, m, 4,5,6-*H* and *Ph*); *m/z* 311 (M^+, 100%) and 296. (Found: C, 69.47; H, 7.08; N, 4.33. $C_{18}H_{21}NSSi$ requires C, 69.40; H, 6.79; N, 4.50%).

η^6-*[1-Methyl-7-(3-methylbut-2-enyl)-2-trimethylsilylindole]tricarbonyl-chromium(0)* [5, E = CHCH=CMe_2]— Eluant: petrol–ether (90:10 → 70:30) gave the *complex* (5, E = CHCH=CMe_2) (530 mg, 43%) as bright orange crystals, m.p. 119–120°C (from petrol–ether); ν_{max} ($CDCl_3$) 1940, 1850, 1440, 1250, 1100, 830 and 625 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 1.8 (6H, br s, CH_2CH=C*Me*$_2$), 3.5–3.8 (2H, m, CH_2CH=CMe_2), 3.9 (3H, s, N-*Me*), 5.0–5.5 (3H, m, 5,6-*H* and CH_2C*H*=CMe_2), 6.15 (1H, dd, *J* 6.2 Hz, 4-*H*) and 6.4 (1H, s, 3-*H*); *m/z* 407 (M^+), 351, 328, 323 (100%) and 271. (Found: C, 59.07; H, 6.25; N, 3.38. $C_{20}H_{25}CrNO_3Si$ requires C, 58.95; H, 6.18; N, 3.44%).

Decomplexation of (5, E = CH(OH)CH=CMe_2) (200 mg, 0.49 mmol) gave *1-methyl-7-(3-methylbut-2-enyl)-2-trimethylsilylindole* (102 mg, 77%) as a colourless crystalline solid, m.p. 106.5–107°C {from petrol (30–40°C) at –78°C}.; $\nu_{max.}$($CHCl_3$) 2960, 2920, 1440, 1305, 1110, 1070, 870, 840 and 660 cm^{-1}; δ_H ($CDCl_3$) 0.35 (9H, s, Si*Me*$_3$), 1.7 (6H, br s, CH_2CH=C*Me*$_2$), 3.75 (2H, d, *J* 7 Hz, CH_2CH=CMe_2), 6.55 (1H, s, 3-*H*) and 6.8–7.6 (3H, m, 4,6-*H*); *m/z* 271 (M^+, 100%), 256, 216 and 198. (Found: C, 74.95; H, 9.05; N, 5.12. $C_{17}H_{25}NSi$ requires C, 75.21; H, 9.28; N, 5.16%).

Desilylation[12] *of 1-methyl-2-trimethylsilylindole* — An ice–cold mixture of trifluoroacetic acid (4.0 g) and water (8.0 g) was added to a solution of 1-methyl-2-trimethylsilylindole (1.40 g, 6.9 mmol) in carbon tetrachloride (10 ml) at 0°C and the mixture stirred vigorously. After 2.5 h, ^1H

NMR analysis indicated complete reaction and the mixture was neutralised with sodium bicarbonate. The aqueous phase was extracted with dichloromethane (2 x 10 ml) and the combined organic phases washed with sodium bicarbonate solution and water before being dried and concentrated to an orange oil. Filtration through silica gel and elution with petrol gave a clear oil (724 mg, 80%) which was identical (TLC, ^{1}H NMR and IR) to authentic 1-methylindole.

Desilylation of 7-ethoxycarbonyl-1-methyl-2-trimethylsilylindole— This was carried out as described above with trifluoroacetic acid (3.0 g), water (1.5 g) and 7-ethoxycarbonyl-1-methyl-2-trimethylsilylindole (623 mg, 2.27 mmol). Work up as above yielded two fractions after chromatography (petrol–ether 100 : 0 → 85 : 15). These were: *7-ethoxycarbonyl-1-methylindole* (244 mg, 53%) as a clear oil, preparative TLC of which gave an analytical pure sample; ν_{max} ($CDCl_3$) 1700, 1320, 1260, 1220, 1200, 1135 and 1105 cm^{-1}; δ_H ($CDCl_3$) 1.4 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 3.85 (3H, s, N-*Me*), 4.4 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 6.55 (1H, d, *J* 3 Hz, 3-*H*), 7.0 (1H, d, *J* 3 Hz, 2-*H*), 7.1 (1H, t, *J* 7 Hz, 5-*H*) and 7.6–7.9 (2H, m, 4,6-*H*); *m/z* 203 (*M*$^+$,100%), 175, 174, 158 and 156. (Found: C, 70.63; H, 6.47; N, 6.70. $C_{12}H_{13}NO_2$ requires C, 70.92; H, 6.45; N, 6.89%); *7-ethoxycarbonyl-2-(7'-ethoxycarbonyl-1'-methylindol-3'-yl)-1-methyl-2,3-dihydroindole* (43 mg, 9%) as an orange oil. ν_{max} ($CDCl_3$) 1700, 1450, 1365, 1200, 1130 and 1095 cm^{-1}; δ_H ($CDCl_3$) 1.4 (6H, dt, 2 overlapping $CO_2CH_2CH_3$), 2.8 (3H, s, N-*Me*), 3.0–3.6 (2H, m, 3-*H*), 3.85 (3H, s, N'-*Me*), 4.4 (4H, m, 2 overlapping $CO_2CH_2CH_3$), 6.7 (1H, t, *J* 7 Hz, 2-*H*) and 7.0–8.0 (7H, m, 4,5,6,2',4',5',6'-*H*); *m/z* 406 (*M*$^+$) and 404 (100%). (Found: *M*$^+$ 406.1881. $C_{24}H_{26}N_2O_4$ requires 406.1892).

η^6-*(1-Methoxymethyl-7-trimethylsilylindole)tricarbonylchromium(0)* (9, R = CH_2OMe, E = $SiMe_3$) — Procedure A but with butyl lithium (1.0 eq) added over a period of 5 min to the indole complex at –98°C. Dilute hydrochloric acid work up, ether extraction and chromatography gave a mixture of 2- and 7-trimethylsilylated complexes (722 mg, 98%) which was crystallised with THF–ether–petrol to give the *complex* (9, R = CH_2OMe, E = $SiMe_3$) (487 mg, 66% overall) as orange crystals, m.p. 121–2°C (from THF–ether–petrol); ν_{max} ($CHCl_3$) 1955, 1875, 1135, 1110, 1040, 840, 660 and 625 cm^{-1}; δ_H ($CDCl_3$) 0.45 (9H, s, $SiMe_3$), 3.25 (3H, s, O*Me*), 4.9 (1H, t, *J* 6 Hz, 5-*H*), 5.35 (2H, q, *J* 12 Hz, CH_2OMe), 5.45 (1H, d, *J* 6 Hz, 6-*H*), 6.35 (1H, d, *J* 3 Hz, 3-*H*), 6.45 (1H, d, *J* 6 Hz, 4-*H*) and 7.15 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 369 (*M*$^+$), 338, 313, 285, 270 and 255 (100%). (Found: C, 51.97; H, 5.15; N, 3.77. $C_{16}H_{19}CrNO_4Si$ requires C, 52.02; H, 5.18; N, 3.79%).

Decomplexation of (9, R = CH_2OMe, E = $SiMe_3$) gave *1-methoxymethyl-7-trimethylsilylindole* (225 mg, 89%) as a clear oil, preparative TLC of which gave analytically pure material; ν_{max} ($CDCl_3$) 2940, 2900, 1520, 1410, 1375, 1300, 1250, 1210, 1185, 1090, 830 and 640 cm^{-1}; δ_H ($CDCl_3$) 0.46 (9H, s, $SiMe_3$), 3.16 (3H, s, O*Me*), 5.57 (2H, s, CH_2OMe), 6.6 (1H, d, *J* 3 Hz, 3-*H*), 7.12 (1H, t, *J* 5 Hz, 5-*H*), 7.2 (1H, d, *J* 3 Hz, 2-*H*), 7.44 (1H, dd, *J* 10, 1.5 Hz, 6-*H*) and 7.66 (1H, dd, *J* 10, 1.5 Hz, 4-*H*); *m/z* 233 (*M*$^+$), 218, 203, 188 and 144 (100%). (Found: C, 66.71; H, 8.27; N, 5.88. $C_{13}H_{19}NOSi$ requires C, 66.90; H, 8.21; N, 6.00%).

η^6-*[1-Methoxymethyl-7-(3-methylbut-2-enyl)indole]tricarbonyl-chromium(0)* [9, R = CH_2OMe, E = $CH_2CH{=}CMe_2$] — Procedure A followed by dilute hydrochloric acid work up, ether extraction and chromatography gave the *complex* (9, R = CH_2OMe, E = $CH_2CH{=}CMe_2$) (720 mg, 49%) as bright yellow crystals, m.p. 102.5–103°C (from THF–ether–petrol); ν_{max} ($CDCl_3$) 2910, 1945, 1860, 1290, 1180, 1110 and 615 cm^{-1}; δ_H ($CDCl_3$) 1.75 (6H, s, $CH_2CH{=}CMe_2$), 3.25 (3H, s, O*Me*), 3.7 and 3.95 (2H, d, *J* 7 Hz, $CH_2CH{=}CMe_2$), 5.0–5.7 (5H, m, 5,6-*H*, $CH_2CH{=}CMe_2$ and

NCH_2O), 6.1 (1H, dd, *J* 6.1 Hz, 4-*H*), 6.35 (1H, d, *J* 3 Hz, 3-*H*) and 7.15 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 365 (*M*$^+$), 309, 281 and 249 (100%). (Found: C, 59.32; H, 5.25; N, 3.96. $C_{18}H_{19}CrNO_4$ requires C, 59.18; H, 5.24; N, 3.83%).

Decomplexation of (**9**, R = CH_2OMe, E = $CH_2CH{=}CMe_2$) (440 mg, 1.2 mmol) gave *1-methoxymethyl-7-(3-methylbut-2-enyl)indole* (251 mg, 91%) as a clear oil, preparative TLC of which gave analytically pure material; ν_{max} ($CDCl_3$) 2930, 1440, 1420, 1370, 1300, 1210, 1180, 1115, 1085 and 635 cm^{-1}; δ_H ($CDCl_3$) 1.75 (6H, s, $CH_2CH{=}CMe_2$), 3.2 (3H, s, O*Me*), 3.8 (2H, d, *J* 6 Hz, $CH_2CH{=}CMe_2$), 5.35 (1H, t, *J* 6 Hz, $CH_2CH{=}CMe_2$), 5.45 (2H, s, NCH_2O), 6.5 (1H, d, *J* 3 Hz, 3-*H*) and 7.0–7.7 (4H, m, 2,4,5,6-*H*); *m/z* 229 (*M*$^+$), 197, 182 (100%) and 154. (Found: C, 78.33; H, 8.30; N, 6.10. $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11%).

Tricarbonyl-(η^6*-2-trimethylsilylindole)chromium(0)* (**8**, R = H, E = $SiMe_3$)— Butyl lithium (1.0 eq) was added to a solution of indole complex (**7**, R = H) (1.228 g, 4.85 mmol) in THF (50 ml) at –20°C. After 30 minutes, dry carbon dioxide was bubbled through the solution for 15 min and the mixture allowed to warm slowly to room temperature whilst being concentrated. Cold THF (50 ml, –78°C) was added *via* a cannula, followed dropwise by butyl lithium (1.1 eq). After 1 h at –78°C, chlorotrimethylsilane (0.68 ml, 1.1 eq) was added and allowed to react at –78°C for 30 min. Water was added and the mixture allowed to warm to room temperature whereupon it was extracted with ether (3 x 50 ml). The combined ethereal phases were dried, concentrated and purified by dry flash chromatography with petrol–ether (2 : 1) as eluant to give the *complex* (**8**, R = H, E = $SiMe_3$) as an orange crystalline solid (1.13 g, 83%) m.p. 105–109°C (dec.); ν_{max} ($CDCl_3$) 3480, 2962, 1961, 1887, 1441, 1254, 1106 and 952 cm^{-1}; δ_H ($CDCl_3$) 0.3 (9H, s, Si*Me*$_3$), 5.05 (1H, t, *J* 6 Hz, 6-*H*), 5.42 (1H, t, *J* 6 Hz, 5-*H*), 6.09 (1H, d, *J* 6 Hz, 7-*H*), 6.38 (1H, d, *J* 6 Hz, 4-*H*), 6.53 (1H, s, 3-*H*) and 7.75 (1H, br s, N-*H*); *m/z* 325(*M*$^+$), 369, 241 and 189. (Found: C, 51.77; H, 4.66; N, 4.27. $C_{14}H_{15}CrNO_3Si$ requires C, 51.68; H, 4.65; N, 4.31%).

General method for preparation of 1-(2-trimethylsilylethoxymethyl)indole complexes.[16] — Sodium hydride (1.2 eq) was suspended in dry DMF (5 ml) and cooled to –20°C. A solution of indole complex in dry DMF (5 ml) at –20°C was added dropwise *via* a cannula and the mixture stirred for 1 h at –20°C, after which 2-trimethylsilylethoxymethyl chloride (SEM-Cl, 1.2 eq) was added and the mixture stirred for a further 1 h at –20°C. Aqueous buffer solution (pH 7) was added, the solution allowed to warm to room temperature and then extracted with ether (2 x 50 ml). The combined ethereal phases were washed with water (25 ml), dried, concentrated and purified by column chromatography, eluant: petrol–ether mixtures. Thus prepared were:—

Tricarbonyl-[η^6*-1-(2-trimethylsilylethoxymethyl)indole]chromium(0)* (**10**, $R^1 = R^2$ =H)— From indole complex (**7**, R = H) (500 mg, 1.97 mmol); the *complex* (**7**, R = SEM) was obtained as a yellow crystalline solid (730 mg, 96%), m.p. 89–90°C.; ν_{max} ($CDCl_3$) 1963 and 1888 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 0.0 (9H, s, Si*Me*$_3$), 0.97 (2H, m, CH_2Si), 3.55 (2H, m, CH_2O), 5.14 (1H, t, *J* 6.4 Hz, 5-*H*), 5.36 (1H, t, *J* 6.4 Hz, 6-*H*), 5.4 and 5.25 (2H, ABq, *J* 11.3 Hz, OCH_2N), 6.20 (1H, d, *J* 6.6 Hz, 7-*H*), 6.28 (1H, d, *J* 6.6 Hz, 4-*H*), 6.36 (1H, d, *J* 3.3 Hz, 3-*H*) and 7.15 (1H, d, *J* 3.5 Hz, 2-*H*); *m/z* 383 (*M*$^+$), 299, 266, 247, 183, 130, 73, 52 and 28. (Found: C, 53.14; H, 5.55; N, 3.49. $C_{17}H_{21}CrNO_4Si$ requires C, 53.26; H, 5.52; N, 3.65%).

Tricarbonyl-[η^6*-1-(2-trimethylsilylethoxymethyl)-2-trimethylsilylindole]chromium(0)* (**10**, R^1 = $SiMe_3$, R^2 = H)— From 2-trimethylsilylindole complex (**8**, R = H, E = $SiMe_3$) (580 mg, 1.78 mmol) the *complex* (**10**, R^1 = $SiMe_3$, R^2 = H) was obtained as a red solid (627 mg, 77%) which was crystallised from petrol to m.p. 62–63°C (softens at 55°C); ν_{max} ($CDCl_3$) 2958, 1955, 1877, 1449,

1288, 1253 and 1085 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.39 (9H, s, 2-Si*Me*$_3$),1.0 (2H, m, C*H*$_2$Si), 3.6 (2H, m, OC*H*$_2$), 5.05 (1H, t, *J* 5 Hz, 6-*H*), 5.2–5.5 (3H, m, 5-*H*, NC*H*$_2$O), 6.10 (1H, d, *J* 6.5 Hz, 7-*H*), 6.30 (1H, d, *J* 6.5 Hz, 4-*H*), 6.5 (1H, s, 3-*H*). (Found: C, 52.86; H, 6.40; N, 3.21. $C_{20}H_{29}CrNO_4Si_2$ requires C, 52.73; H, 6.42; N, 3.07%).

η^6*-[3-Methyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonyl-chromium(0)* (**10**, R^1 = H, R^2 = Me)— From 3-methylindoletricarbonylchromium(0) (1 g, 3.74 mmol), the *complex* (**10**, R^1 = H, R^2 = Me) was obtained as a yellow crystalline solid (1.442 g, 97%) m.p. 92–93°C; ν_{max} ($CDCl_3$) 2956, 2924, 1955, 1876, 1455, 1325, 1252, 1125 and 1082 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, Si*Me*$_3$), 0.95 (2H, m, C*H*$_2$Si), 2.1 (3H, s, *Me*), 3.5 (2H, m, OC*H*$_2$), 5.1–5.4 (4H, m, NC*H*$_2$O, 5,6-*H*), 6.2 (2H, t, 4,7-*H*) and 6.9 (1H, s, 2-*H*); *m/z* 397 (*M*$^+$), 313, 280, 223, 197 and 149 (100%). (Found: C, 54.40; H, 5.81; N, 3.60. $C_{18}H_{23}CrNO_4Si$ requires C, 54.38; H, 5.83; N, 3.52%)

General procedure for the lithiation of 1-(2-trimethylsilylethoxymethyl)indole complexes:— Procedure A was followed by work up with aqueous pH 7.0 buffer solution. The mixture was extracted with ether (2 x 25 ml) and the combined ethereal phases dried and concentrated to a red oil which was purified by column chromatography. Thus prepared were:—

Tricarbonyl-[η^6*-2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]chromium(0)* (**10**, R^1 = $SiMe_3$, R^2 = H) *and tricarbonyl-[η*^{6}*-7-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]-chromium(0)* (**11**, R^1 = R^2 = H, E = $SiMe_3$) — Butyl lithium (1.0 eq) was added over 5 min to give, after quenching with chlorotrimethylsilane, work up, and chromatography, an inseparable mixture of the 2- and 7-trimethylsilylated complexes (**10**, R^1 = $SiMe_3$, R^2 = H) and (**11**, R^1 = R^2 = H, E = $SiMe_3$) in a 1 : 1 ratio, determined by 270 MHz ^{1}H NMR spectroscopy by comparison with the spectrum of authentic 2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole complex (*vide supra*).

η^6*-[7-Methyl-2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonylchromium(0)* (**11**, R^1 = $SiMe_3$, R^2 = H, E = Me) — 2-Trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole complex (**10**, R^1 = $SiMe_3$, R^2 = H) (150 mg, 0.329 mmol), after lithiation and quenching with excess methyl iodide, gave the *complex* (**11**, R^1 = $SiMe_3$, R^2 = H, E = Me) as an orange oil (146 mg, 95%); ν_{max} ($CDCl_3$) 2957, 1951, 1872, 1463, 1395, 1293, 1254, 1072 and 842 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.4 (9H, s, 2-Si*Me*$_3$), 1.0 (2H, m, C*H*$_2$Si), 2.8 (3H, s, 7-*Me*), 3.6 (2H, m, OC*H*$_2$), 5.15 (2H, m, 5,6-*H*), 5.35, 5.54 (2H, ABq, *J* 8.3 Hz, OC*H*$_2$N), 6.07 (1H, dd, *J* 8.4, 1.7 Hz, 4-*H*) and 6.5 (1H, s, 3-*H*); *m/z* 469 (*M*$^+$), 413, 385 and 269; (Found: 469.1195 $C_{21}H_{31}CrNO_4Si$ requires 469.1196)

η^6*-[7-Formyl-2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonylchromium(0)* (**11**, R^1 = $SiMe_3$, R^2 = H, E = CHO), — 2-Trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole complex (**10**, R^1 = $SiMe_3$, R^2 = H) (135 mg, 0.296 mmol), after lithiation and quenching with excess DMF, gave the *complex* (**11**, R^1 = $SiMe_3$, R^2 = H, E = CHO) as a bright red oil (101 mg, 70%);ν_{max} (CCl_4) 2957, 1978, 1898, 1691, 1367, 1253 and 1081 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.4 (9H, s, 2-Si*Me*$_3$), 1.1 (2H, 2t, *J* 7 Hz, C*H*$_2$Si), 3.5 (2H, m, OC*H*$_2$), 5.05 (1H, t, *J* 6 Hz, 5-*H*), 5.4, 5.8 (2H, ABq, *J* 10.4 Hz, OC*H*$_2$N), 6.1 (1H, d, *J* 6.1 Hz, 6-*H*), 6.6 (2H, overlapping s and d, 2,4-*H*) and 10.1 (1H, s, C*H*O); *m/z* 483 (*M*$^+$). (Found: 483.0993. $C_{21}H_{29}CrNO_5Si_2$ requires 483.0989).

η^6*-[3-Methyl-7-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonylchromium(0)* (**11**, R^1 = H, R^2 = Me, E = $SiMe_3$)— 3-Methyl-1-(2-trimethylsilylethoxymethyl)indole complex (**10**,

R^1 = H, R^2 = Me) (266 mg, 0.697 mmol) after lithiation and quenching with chlorotrimethylsilane gave the *complex* (11, R^1 = H, R^2 = Me, E = $SiMe_3$) as a red crystalline solid (278 mg, 88%), m.p. 109–110°C (from petrol–ether at 0°C); ν_{max} ($CDCl_3$) 2957, 1953, 1875, 1416, 1253, 1078, 864 and 839 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.6 (9H, s, 2-Si*Me*$_3$), 0.9 (2H, t, *J* 8.4 Hz, C*H*$_2$Si), 2.1 (3H, s, 3-*Me*), 3.4 (2H, m, OC*H*$_2$), 4.95 (1H, t, *J* 6.4 Hz, 5-*H*), 5.5 (1H, d, *J* 6 Hz, 6-*H*), 5.5, 5.2 (2H, ABq, *J* 11 Hz, OC*H*$_2$N), 6.4 (1H, d, *J* 6.4 Hz, 4-*H*) and 6.9 (1H, s, 2-*H*); *m/z* 469 (*M*$^+$), 385 and 269 (100%). (Found: C, 53.79; H, 6.58; N, 3.04. $C_{21}H_{31}CrNO_4Si_2$ requires C, 53.71; H, 6.65; N, 2.98%).

η^6-*[7-Ethoxycarbonyl-3-methyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonylchromium(0)* (11, R^1 = H, R^2 = Me, E = CO_2Et) — 3-Methyl-1-(2-trimethylsilylethoxymethyl)indole complex (10, R^1 = H, R^2 = Me) (250 mg, 0.628 mmol) after lithiation and quenching with an excess of ethyl chloroformate gave the *complex* (11, R^1 = H, R^2 = Me, E = CO_2Et) as lustrous red crystals (195 mg, 66%), m.p. 100–101°C; ν_{max} ($CDCl_3$) 2957, 1966, 1897, 1714, 1510, 1445, 1392, 1373, 1265, 1251, 1184, 1087, 861 and 838 cm^{-1}; δ_H ($CDCl_3$) –0.05 (9H, s, Si*Me*$_3$), 0.8 (2H, s, C*H*$_2$Si), 1.4 (3H, t, *J* 7.3 Hz, C*H*$_3$CH$_2$), 2.23 (3H, d, *J* 1 Hz, 3-*Me*), 3.3 (2H, m, OC*H*$_2$), 4.4 (2H, m, OC*H*$_2$), 5.03 (1H, d, *J* 10.4 Hz, NC*H*$_2$O), 6.0–6.05 (2H, dd and d, *J* 6.2, 1.1, 10.4 Hz, 7-*H* and NC*H*$_2$O) 6.34 (1H, dd, *J* 6.4, 1 Hz, 4-*H*) and 6.96 (1H, d, *J* 1 Hz, 2-*H*); *m/z* 469 (*M*$^+$), 385, 352, 333, 269, 254, 216, 157, 73, 52 and 28. (Found: C, 53.60; H, 5.76; N, 2.94. $C_{21}H_{27}CrN0_6Si$ requires C, 53.72; H, 5.79; N, 2.98%).

η^6-*[3-Methyl-1-(2-trimethylsilylethoxymethyl)-7-trimethylstannyl)indole]tricarbonylchromium(0)* (11, R^1 = H, R^2 = Me, E = $SnMe_3$). — 3-Methyl-1-(2-trimethylsilylethoxymethyl)indole complex (10, R^1 = H, R^2 = Me) (140 mg, 0.35 mmol) gave, after lithiation and quenching with chlorotrimethylstannane, the *complex* (11, R^1 = H, R^2 = Me, E = $SnMe_3$) as a pale yellow solid (125 mg, 65%). An analytically pure sample was obtained by crystallisation from petrol at –78°C, m.p. 108–109°C; ν_{max} ($CDCl_3$) 2956, 1951, 1871, 1251 and 1077 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, Si*Me*$_3$), 0.5 (9H, s + d, $J_{Sn\text{-}H}$ 112 Hz, Sn*Me*$_3$), 0.9 (2H, s, C*H*$_2$Si), 2.1 (3H, s, 3-*Me*), 3.5 (2H, m, OC*H*$_2$), 5.03 (1H, t, *J* 6.5 Hz, 5-*H*), 5.34 (2H, ABq, *J* 11 Hz, NC*H*$_2$O), 5.3 (1H, dd, *J* 6.5, 1 Hz, 6-*H*), 6.34 (1H, dd, *J* 6.5, 1.2 Hz, 4-*H*) and 6.82 (1H, d, *J* 1.2 Hz, 2-*H*); *m/z* 565, 561, 559, 557 (*M*$^+$), 44, 361, 345, 311, 195 and 73. (Found: C, 44.78; H, 5.48; N, 2.44. $C_{21}H_{31}CrNO_4SiSn$ requires: C, 45.02; H, 5.58; N, 2.50%).

η^6-*[3-Methyl-2,7-di-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]-tricarbonylchromium(0)* (11, R^1 = E = $SiMe_3$, R^2 = Me). — 3-Methyl-7-trimethylsilyl-1-SEM-indole complex (11, R^1 = H, R^2 = Me, E = $SiMe_3$) (159 mg, 0.338 mmol) after lithiation and quenching with chlorotrimethylsilane gave the *complex* (11, R^1 = E = $SiMe_3$, R^2 = Me) as an orange crystalline solid (151 mg, 82%), m.p. 84–85°C; δ_H (270 MHz, $CDCl_3$) –0.1 (9H, s, SEM-Si*Me*$_3$), 0.4 (9H, s, 7-Si*Me*$_3$), 0.6 (9H, s, 2-Si*Me*$_3$), 0.9 (2H, m, C*H*$_2$Si), 2.12 (3H, s, 3-*Me*), 3.1, 2.9 (2H, m, OC*H*$_2$), 4.88 (1H, t, *J* 6.4 Hz, 5-*H*), 5.3 (2H, ABq, *J* 11 Hz, NC*H*$_2$O), 5.52 (1H, d, *J* 6.1 Hz, 6-*H*) and 6.37 (1H, d, *J* 6.4 Hz, 4-*H*); *m/z* (20 ev) 541 (*M*$^+$), 457, 405, 341 and 289. (Found: C, 53.39; H, 7.38; N, 2.59. $C_{24}H_{39}CrNO_4Si_3$ requires C, 53.20; H, 7.26; N, 2.59%).

General procedure for formation of aryl copper species and subsequent reaction:— The indole complex was lithiated as in procedure A and the lithio- intermediate treated with copper bromide–dimethyl sulfide complex (1.1 eq) *via* a solids addition tube and the mixture warmed to –20°C for 1h. Excess electrophile was added and the mixture stirred for a further 1h at –20°C then

allowed to warm to room temperature over the time period specified. Aqueous pH 7.0 buffer solution was added and the mixture extracted with ether (3 x 50 ml). The combined ethereal phases were dried, concentrated and chromatographed. So prepared were:—

η^6-[7-Prop-2-enyl-2-trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole]tricarbonyl-chromium(0) (11, R^1 = $SiMe_3$, R^2 = H, E = $CH_2CH{=}CH_2$). — 2-Trimethylsilyl-1-(2-trimethylsilylethoxymethyl)indole complex (10, R^1 = $SiMe_3$, R^2 = H) (300 mg, 0.658 mmol) on metallation and quenching with allyl bromide, gave the *complex* (11, R^1 = $SiMe_3$, R^2 = H, E = $CH_2CH{=}CH_2$) (225 mg, 69%) as a red solid, m.p. 78–80°C; ν_{max} ($CDCl_3$) 2957, 1952, 1875, 1253 and 1077 cm^{-1}; δ_H ($CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.4 (9H, s, 2-Si*Me*$_3$), 1.0 (2H, m, C*H*$_2$Si), 3.5 (2H, m, OC*H*$_2$), 3.72 (1H, dd, *J* 16.2, 5.4 Hz, ArC*H*), 4.1 (1H, dd, *J* 16.4, 6.4 Hz, ArC*H*), 5.4–5.0 (6H, m, NC*H*$_2$O, 5,6-*H* and C*H*$_2$=CH), 6.2–6.1 (2H, m, 4-*H* and CH_2=C*H*) and 6.5 (1H, s, 3-*H*); *m/z* 495 (*M*+), 411, 359, 295, 241 and 73. (Found: C, 55.77; H, 6.78; N, 2.79. $C_{23}H_{33}CrNO_4Si_2$ requires C, 55.73; H, 6.71; N, 2.83%).

Also isolated was the decomplexed product, *7-(prop-2-enyl)-1-(2-trimethylsilylethoxymethyl)-2-trimethylsilylindole* (68 mg, 29%) as a clear oil, identified by nOe experiments; δ_H (250 MHz, $CDCl_3$) 0.0 (9H, s, SEM-Si*Me*$_3$), 0.4 (9H, s, 2-Si*Me*$_3$), 1.0 (2H, t, *J* 7 Hz, C*H*$_2$Si), 3.5 (2H, t, *J* 7 Hz, OC*H*$_2$), 3.9 (2H, d, *J* 5.4 Hz, ArC*H*$_2$), 4.9 (1H, dd, *J* 16.5, 1.7 Hz, CH=C*H*$_2$), 5.15 (1H, dd, *J* 10, 1.7 Hz, CH=C*H*$_2$), 5.55 (2H, s, NC*H*$_2$O), 6.4 (1H, m, C*H*=CH$_2$), 6.8 (1H, s, 3-*H*), 7.2 (2H, m, 5,6-*H*) and 7.5 (1H, dd, *J* 7, 1.7 Hz, 4-*H*); *m/z* 359 (*M*+), 319, 241, 202 and 73 (100%). (Found: *M*+ 359.2106; $C_{20}H_{33}NOSi_2$ requires 359.2100)

η^6-[3-Methyl-7-(prop-2-enyl)-1-(2-trimethylsilylethoxymethyl)indole]tricarbonylchromium(0) (11, R^1 = H, R^2 = Me, E = $CH_2CH{=}CH_2$)— 3-Methyl-1-(2-trimethylsilylethoxymethyl)indole complex (10, R^1 = H, R^2 = Me) (245 mg, 0.64 mmol) on metallation and quenching with allyl bromide, gave the *complex* (11, R^1 = H, R^2 = Me, E = $CH_2CH{=}CH_2$)as a yellow crystalline solid (212 mg, 79%) m.p. 114–116°C (softens at 100–105°C); *m/z* 437 (*M*+), 353 and 237. (Found: C, 57.45; H, 6.13; N, 3.1. $C_{21}H_{27}CrNO_4Si$ requires C, 57.65; H, 6.22; N, 3.20%).

η^6-[7-(But-2-en-2-yl)-3-methyl-1-(2-trimethylsilylethoxymethyl)indole]-tricarbonylchromium(0) (11, R^1 = H, R^2 = Me, E = C(Me)=CHMe). — 3-Methyl-1-(2-trimethylsilylethoxymethyl)indole complex (10, R^1 = H, R^2 = Me) (250 mg, 0.63 mmol) was lithiated as above and copper bromide dimethyl sulphide complex (1.05 eq) added and the mixture warmed to –23°C, and stirred for 1 h. Tetrakistriphenylphosphinepalladium(0) (10 mol %) and 2-bromobut-2-ene (3 eq) were added and the reaction mixture allowed to warm to room temperature and stirred for 2 h. The resulting solution was filtered through a pad of silica gel, washed sequentially with water and brine, drying and the solvent evaporated to give an orange oil. Further purification by column chromatography gave the *complexes* (11, R^1 = $SiMe_3$, R^2 = H, E = C(Me)=CHMe) (194 mg, 68%); δ_H (270 MHz, $CDCl_3$) 0.00 (9H, s, Si*Me*$_3$), 0.90 (2H, m, C*H*$_2$Si), 1.40 and 1.85 (3H, dd, *J* 7.2, 2 Hz, *Me*CH=), 2.2 and 2.4 (6H, s, 3-*Me* and *Me*C[Ar]=), 3.40 (2H, m, OC*H*$_2$), 4.95 (1H, t, *J* 6.7 Hz, 5-*H*), 5.30 (2H, d, *J* 7 Hz, 6-*H*, + ABq, *J* 10.7 Hz, NC*H*$_2$O), 5.90 and 6.20 (1H, dq, *J* 7, 2 Hz, MeC*H*=), 6.25 (1H, d, *J* 6.7 Hz, 4-*H*) and 6.9 (1H, s, 2-*H*); *m/z* 451 (*M*+), 395, 367 and 315. (Found: *M*+, 451.1278; $C_{22}H_{29}CrNO_4Si$ requires 451.1277).

Control Experiments.—

a) *3-Methyl-1-(2-trimethylsilylethoxymethyl)indole* was prepared by the method previously described[16], as an oil, in 87% yield; δ_H (270 MHz, $CDCl_3$) 0.10 (9H, s, Si*Me*$_3$), 0.9 (2H, t, *J* 7 Hz,

CH_2Si), 2.30 (3H, s, 3-*Me*), 3.5 (2H, t, *J* 7 Hz, OCH_2), 5.4 (2H, s, NCH_2O), 6.95 (1H, s, 2-*H*), 7.18 (2H, m, 5,6-*H*), 7.4 (1H, d, *J* 7.5 Hz, 7-*H*) and 7.6 (1H, d, *J* 7.5 Hz, 4-*H*); *m/z* 261 (M^+), 231, 203, 188, 147, 144, 103 and 73. (Found: C, 68.77; H, 9.10; N, 5.32. $C_{15}H_{23}NOSi$ requires: C, 68.92; H, 8.87; N, 5.36%).

b) Butyl lithium (1.1 eq) was slowly added dropwise to a solution of 3-methyl-1-(2-trimethylsilylethoxymethyl)indole (253 mg, 0.96 mmol) in dry 1,2-dimethoxyethane (5 ml) at –23°C. After 15 min, excess chlorotrimethylsilane was added in one portion and the mixture stirred at –23°C for 1 h. The solution was partitioned between aqueous pH 7.0 buffer and ether and the organic phase separated, dried and evaporated. The residue was chromatographed over silica gel to give, in order of elution: *3-methyl-2-trimethylsilyl-1-(2-trimethylsilylethoxymehtyl)indole* (114 mg, 35%); ν_{max} ($CDCl_3$) 2956, 2898, 1455, 1412, 1386, 1353, 1308, 1251 and 1069 cm^{-1}; δ_H (270 MHz, $CDCl_3$) –0.20 (9H, s, SEM-Si*Me*$_3$), 0.42 (9H, s, 2-Si*Me*$_3$), 0.90 (2H, t, *J* 7 Hz, CH_2Si), 2.40 (3H, s, 3-*Me*), 3.40 (2H, t, *J* 7 Hz, OCH_2), 5.5 (2H, s, NCH_2O), 7.1 (1H, t, *J* 7.6 Hz, 6-*H*), 7.2 (1H, t, *J* 7.6 Hz, 5-*H*), 7.4 (1H, d, *J* 7.6 Hz, 7-*H*) and 7.55 (1H, d, *J* 7.6 Hz, 4-*H*); *m/z* 333 (M^+), 260, 216 and 73 (100%). (Found: C, 64.71; H, 9.28; N, 4.28. $C_{18}H_{31}NOSi_2$ requires: C, 64.81; H, 9.37; N,4.20%); and recovered starting material, (100 mg, 40%).

General Procedure for the Removal of the 2-Trimethylsilylethoxymethyl Group. — Freshly prepared anhydrous tetrabutylammonium fluoride (≈10 eq) was added dropwise to a solution of the 1-(2-trimethylsilylethoxymethyl)indole complex (0.25 mmol) in dry THF (2 ml) at 0°C and the solution stirred at that temperature until t.l.c. analysis indicated the complete consumption of substrate (4–7 h). The reaction mixture was partitioned between XX% aqueous ammonium chloride (5 ml) and ether (2 x 10 ml). The combined ethereal phases were dried ($MgSO_4$), preadsorbed on to silica gel and the products purified by dry flash column chromatography on elution with petrol : ether.

So prepared were indoletricarbonylchromium(0) (61.2 mg, 62%) and 3-methylindoletricarbonylchromium(0) (50.7 mg, 71%), each identical by p.m.r., i.r., m.s., and t.l.c. with authentic specimens, and (E/Z)-η^6-*[7-(but-2-en-2yl)-3-methylindole]tricarbonylchromium(0)*; ν_{max} ($CHCl_3$) 3463, 2922, 1951, 1870, 1723, 1593 and 1079 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 1.5 and 1.9 (3H, d, *J* 13 Hz, *Me*CH=), 2.26 (3H, s, 3-*Me*), 2.18 and 2.3 (3H, s, *Me*CH[Ar]=), 4.95 and 5.09 (1H, t, *J* 6.7 Hz, 5-*H*), 5.4 and 5.48 (1H, d, *J* 6.7 Hz, 6-*H*), 5.9 and 6.15 (1H, q, *J* 13 Hz, MeC*H*=), 6.25 and 6.3 (1H, d, *J* 6.7 Hz, 4-*H*), 6.9 (1H, s, 2-*H*) and 7.4 and 7.8 (1H, br. s, N-*H*); *m/z* 321 (M^+), 265, 237, 185 and 52. [Found: $(M + H)^+$ (NH_3, CI) 322.0535. $C_{16}H_{16}CrNO_3$ requires 322.0535].

REFERENCES

1. J.V. Greenhill in 'Comprehensive Heterocyclic Chemistry', eds. A.R. Katritsky and C.W. Rees, Pergamon Press, Oxford, 1984, vol. 4, p. 497.
2. J.H. Cardellina, F.J. Marner and R.E. Moore, *Science*, 1979, **204**, 193.
3. Y. Hitotsuyanagi, H. Fujiki, M. Suganuma, N. Aimi, S. Sakai, Y. Endo, K. Shudo and T. Sugimura, *Chem. Pharm. Bull. (Japan)*, 1984, **32**, 4233.
4. P.J. Beswick, C.S. Greenwood, T.J. Mowlem, G. Nechvatal and D.A. Widdowson, *Tetrahedron*, 1988, **44**, 7325.
5. For a preliminary report of this work, see G. Nechvatal, D.A. Widdowson and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 1260.
6. M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W.D. Wulff and Y. Yamashita, *Tetrahedron*, 1981, **37**, 3957.

7. A.P. Kozikowski and K. Isobe, *J. Chem. Soc., Chem. Commun.*, 1978, 1076; see also M.F. Semmelhack, W, Wulff and J.L. Garcia, *J. Organomet. Chem.*, 1982, **240**, C5.
8. *a.* (1-Methylindole series) D.A. Shirley and P.A. Roussel, *J. Am. Chem. Soc.*, 1953, **75**, 375; *b.* (1-Boc-indole series) I. Hasan, E.R. Marinelli, L. Chin, E.W. Fowler and A.B. Levy, *J. Org. Chem.*, 1981, **46**, 157; *c.* (1-arylsulphonylindole series) R.J. Sundberg And H.F. Russell, *J. Org. Chem.*, 1973, **38**, 3324.
9. For details of the crystal data, see ref 5, footnote §.
10. For a more detailed study, see J.P. Gilday, PhD Thesis, University of London, 1986.
11. (Photo-oxidative decomplexation) A.J. Birch, P.E. Cross, D.T. Connor and G.S.R. Subba Rao, *J. Chem. Soc.*, 1966, 54; G. Jaouen and R. Dabard, *Tetrahedron Lett.*, 1971, 1015; (pyridine decomplexation) G. Carganico, P. del Buttero, S. Maiorana and G. Riccardi, *J. Chem. Soc., Chem. Commun.*, 1978, 989; (oxidative decomplexation) M.F. Semmelhack and H.T. Hall, *J. Am. Chem. Soc.*, 1974, **96**, 7091; W.S. Trahanovsky and R.J. Card, *J. Am. Chem. Soc.*, 1972, **94**, 2897.
12. C. Eaborn, P.M. Jackson and R. Taylor, *J. Chem. Soc. B*, 1966, 613.
13. H.W. Gschwend and H.R. Rodriguez, *Org. React.*, 1979, **26**, 1.
14. For details of methoxymethyl group removal, see ref. 8c and references there cited.
15. T.R. Kelly, H.M. Dali and W.-G. Tsang, *Tetrahedron Lett.*, 1977, **18**, 3859.
16. M.P. Edwards, A.M. Doherty, S.V. Ley and H.M. Organ, *Tetrahedron*, 1986, **42**, 3723.
17. A.R. Katritsky and K. Akutagawa, *Tetrahedron Lett.*, 1985, **26**, 5935.
18. C.A.L. Mahaffy and P.L. Pauson, *Inorg. Synth.*, 1979, **19**, 154.
19. W. Ströhmeier, *Chem. Ber.*, 1961, **94**, 2490.