Tetrahedron Vol. 44, No. 23, pp. 7325 to 7334, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00

The Synthesis of 4 - Substituted Indoles *via* Arenetricarbonylchromium(0) Complexes

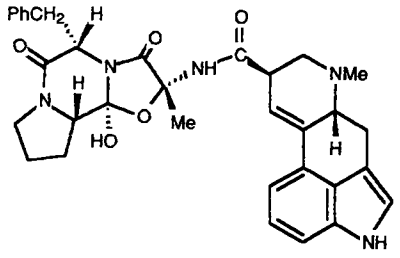
P. J. Beswick, C. S. Greenwood, T. J. Mowlem, G. Nechvatal and D. A. Widdowson*

Department of Chemistry, Imperial College, London SW7 2AY.

(*Received in UK 7 October* 1988)

Abstract – Lithiation of tricarbonyl-η^6-(1-tri-isopropylsilylindole)chromium(0) and η^6-(1-tri-isopropylsilyl-3-methoxymethylindole)tricarbonylchromium(0) followed by an electrophilic quench produced a series of 4-substituted indole complexes. For the 4-acyl, -allyl and -alkenyl analogues, transmetallation of the lithio- species to the corresponding cupro- complexes and reaction with the appropriate halides (in the alkenyl case with palladium catalysis) gave in total, a wide range of 4-substitutents. The complexes were decomplexed and desilylated to produce the 4-substituted indoles in moderate to good overall yield.

The 4-substituted indole nucleus is widespread in nature and is found in *inter alia* the ergot alkaloids[1], the tremorgenic mycotoxins[2] and the indolactam/teleocidin group of compounds[3], all of which show pronounced pharmacological effects and a number of which, such as ergotamine, (**1**), are clinically useful[4].



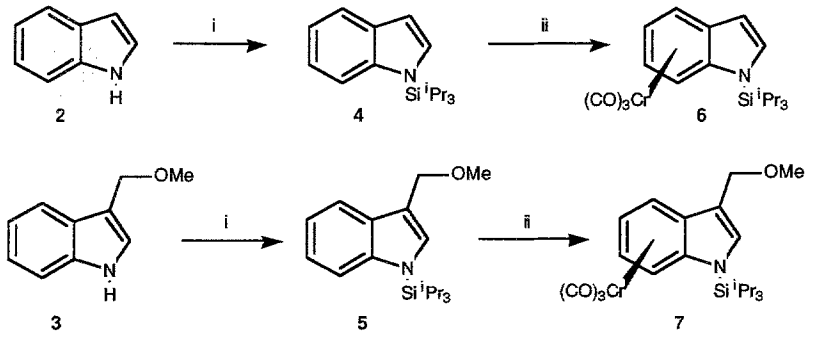
1

Although methods for the introduction of substituents into the 1-, 2- and 3 - positions are well established[5], direct functionalisation of the carbocyclic ring, and in particular the 4- position, has proved more difficult and with few exceptions[6], low yields and complex mixtures are the observed outcome. The most efficient approaches have been those incorporating syntheses from non-indolic starting materials, a number of which have been recently reviewed.[7]

The activation of arenes complexed with tricarbonylchromium(0), especially the increased acidity of the ring protons, is well documented[8] and recently we reported[9] that the lithiation of η^6-(*N*-protected indole)tricarbonylchromium(0) complexes could be effected regioselectively at the 4- position. The use of a bulky *N*-substituent (t-butyldimethylsilyl or tri-isopropylsilyl) afforded lateral protection of the 2- and 7-positions with the *N*-tri-isopropylsilyl derivatives being the more effective. We now demonstrate the generality

of the method for the synthesis of a range of 4-substituted indoles.

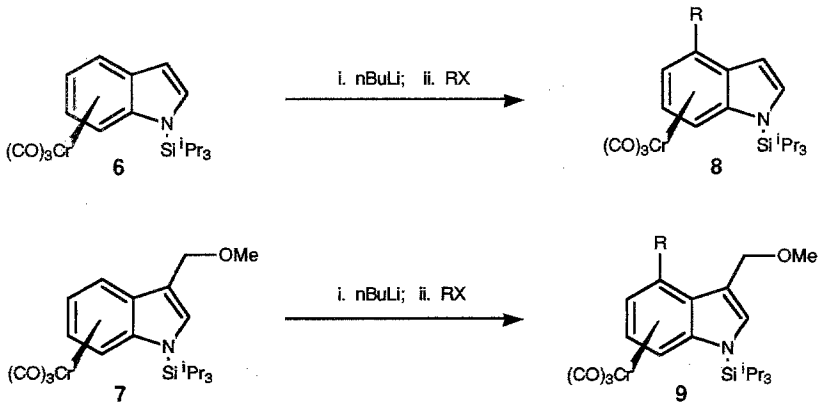
N-Silylation of indole (**2**) and 3-methoxymethylindole (**3**) (1 equivalent n-butyl lithium/chlorotri-isopropylsilane) gave the protected species (**4**) and (**5**) in quantitative and 98% yield respectively. Direct complexation[10] of the *N*-protected indoles (**4**) and (**5**) with hexacarbonylchromium gave the complexes (**6**) and (**7**) in 87% and 72% yield respectively (Scheme 1).



Reagents: i. nBuLi, $ClSi^iPr_3$; ii. $Cr(CO)_6$, nBu_2O - THF (10 : 1).

Scheme 1

The complexes were lithiated with 2 equivalents of n-butyl lithium - TMEDA at -78°C fo 3 h (Scheme 2). The lithiated species could be quenched with a series of electrophiles in good to moderate yields (Table 1). C-4 functionalisation was established from a nuclear Overhauser effect (n.O.e) difference spectrum of the decomplexed 4-trimethylsilylated product[9] (**10**, R = $SiMe_3$). Irradiation of the protons of the trimethylsilyl group at δ 0.45 resulted in the enhancement of the 3-H and 5-H signals at δ 6.75 and δ 7.25 - 7.3 respectively. Irradiation of the tri-isopropylsilyl protons produced an enhancement of the 2-H and 7-H signals at δ 7.25 - 7.3 and δ 7.54 respectively. These observations were consistent only with a 1,4- disubstituted indole derivative.



Scheme 2

Small amounts of the 5- and 6-substituted species were observed in the lithiation of the complex (**6**), but the extra chelation control conferred by the methoxymethyl group in (**7**) allowed specific formation of the 4-substituted products (**11**). Products derived from C-2 and C-7 lithiation were not observed in either case.

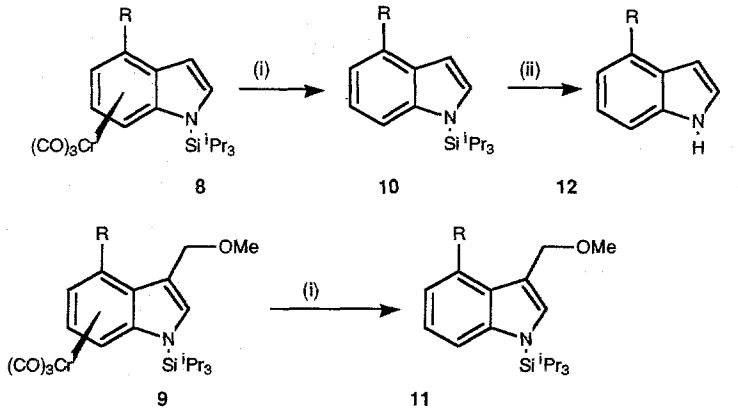
Table 1: 4-Substituted Indole Synthesis from 4- Lithio-indole Complexes (Schemes 2 and 3).

Substrate	Electrophile	Product (%)	Decomplexation (%)	Desilylation (%)
6	$ClSiMe_3$	**8**, R = $SiMe_3$ (56)	**10**, R = $SiMe_3$ (93)[a]	**12**, R = $SiMe_3$ (86)[b]
6	$ClCO_2Me$	**8**, R = CO_2Me (59)	—	**12**, R = CO_2Me (81)[b]
6	$ClCO_2Et$	**8**, R = CO_2Et (60)	**10**, R = CO_2Et (84)[a]	**12**, R = CO_2Et (100)
6	$BrCH_2CH{=}CMe_2$	**8**, R = $CH_2CH{=}CMe_2$(36)	—	**12**, R = $CH_2CH{=}CMe_2$ (95)[b]
6	$ClSnMe_3$	**8**, R = $SnMe_3$ (69)	**10**, R = $SnMe_3$ (90)[a]	—
6	I_2	**8**, R = I (52)	**10**, R = I (100)[a]	—
6	ClSPh	—	—	**12**, R = SPh (26)[b]
7	$ClSiMe_3$	**9**, R = $SiMe_3$ (81)	**11**, R = $SiMe_3$ (92)[a]	—
7	$ClCO_2Me$	**9**, R = CO_2Me (61)	—	—
7	$ClSnMe_3$	**9**, R = $SnMe_3$ (79)	**11**, R = $SnMe_3$ (90)[a]	—
7	I_2	**9**, R = I (66)	**11**, R = I (94)[a]	—

[a] Photolytic decomplexation.

[b] Reaction sequence: i, TBAF desilylation; ii, thermal (pyridine) decomplexation; the overall yield is given.

The complexes shown in Table 1 could be decomplexed [hv, (tungsten lamp)/air[11]]to give, in near quantitative yields, the 4-substituted- *N*-tri-isopropylsilylindoles (**10**) and 3-methoxymethyl-*N*-tri-isopropyl-silylindoles (**11**). Desilylation could be carried out on the (**10**) series with tetrabutylammonium fluoride (TBAF) in THF (Scheme 3). Alternatively, the sequence could be reversed with fluoride desilylation of (**8**) followed by thermal decomplexation (reflux in pyridine) to give the 4-substituted indole derivatives (**12**) in good yields (Table 1).



Reagents: (i) hv / O_2, CH_3CN; (ii) TBAF

Scheme 3

The range of electrophiles with which the 4-lithio-indole complexes would react was found to be

somewhat limited[12]. This is due to their low nucleophilicity relative to their basicity, a property presumably exacerbated by the electron withdrawing nature of the tricarbonylchromium group[8]. Hence proton quenching was a competing reaction. Transmetallation of the 4-lithio species (**8**, R = Li) to the analogous, low basicity, highly reactive copper complexes[13] (**8**, R = $CuSMe_2$) ($CuBr.SMe_2$, 1 equivalent, -23°C) overcame this problem. The 1 : 1 stoicheiometry of indole : copper proved to be the most effective reagent. In this way the 4-substituted indoles derived from the reaction of the copper complex (**8**, R = $CuSMe_2$) with acetyl chloride and *E*-methyl-4-bromo-2-butenoate were achieved in moderate yield. The reaction with prenyl bromide also resulted in an improved yield (51%) of the 4-substituted indole (**8**, R = $CH_2CH{=}CMe_2$).

Table 2: 4-Substituted Indole Synthesis from 4-Cupro-indole Complex (**8**, R = $Cu.SMe_2$).

Electrophile	Product (**8**, R =) (%)	Arene (**10**, R =) (%)
ClCOMe	COMe (45)	—
$BrCH_2CH{=}CMe_2$	$CH_2CH{=}CMe_2$ (51)	$CH_2CH{=}CMe_2$ (95)[a]
$BrCH_2CH{=}CHCO_2Me$	$CH_2CH{=}CHCO_2Me$ (58)	$CH_2CH{=}CHCO_2Me$ (58)
$BrCH{=}CH_2$	$CH{=}CH_2$ (43)[b]	—
$BrC{=}CHCOCH_2CMe_2CH_2$	$C{=}CHCOCH_2CMe_2CH_2$ (34)[b]	—
$BrCH{=}CHCO_2Me$	$CH{=}CHCO_2Me$ (41)[b]	$CH{=}CHCO_2Me$ (97)

[a] Reaction sequence: desilylation - decomplexation, overall yield given.

[b] Palladium catalysis (5 mol %) used.

The range of compatible electrophiles was further extended to include vinyl halides through the use of palladium catalysis[14]. Addition of the halide [vinyl bromide, *trans*-2-methoxycarbonylethenyl or 1-bromo-5,5-dimethylcyclohexene-3-one, (**13**)] and tetrakis(triphenylphosphine) palladium(0) (4 - 5 mol %) to the copper - indole species (**8**, R = $CuSMe_2$) gave the 4-substituted indoles in moderate yields (Table 2).

This combination of chromium induced directed lithiation/electrophilic quench, directed lithiation/transmetallation/electrophilic quench or directed lithiation/transmetallation/palladium catalysed cross coupling gives access to a wide range of 4- substituted indoles not readily accessible by conventional direct methods.

ACKNOWLEDGEMENTS.

We thank the Johnson Matthey Company for the loan of palladium chloride, the Science and Engineering Research Council for the award of studentships to PJB, TJM and GN and the Commonwealth Commission for the award of a Studentship to CSG.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 grating spectrometer or a Perkin-Elmer model 1710 FT spectrometer and mass spectra on a VG 7070 spectrometer. ^{1}H-nmr were recorded at 90 MHz (Perkin-Elmer R32 spectrometer) or at 250 MHz (Bruker WH-250FT spectrometer) with tetramethylsilane as an internal standard. Petrol refers to the fraction b.p. 40-60°C unless otherwise stated. THF was dried by distillation from sodium - potassium - benzophenone ketyl; di-n-butyl ether was distilled from sodium. Reactions involving chromium tricarbonyl complexes or alkyl lithiums were performed under an atmosphere of dry oxygen-free nitrogen. Organic solvents were routinely dried over anhydrous magnesium sulphate. Column chromatography was performed using Rose Chemicals silica gel H. Thin layer chromatography and preparative t.l.c. were carried

out using plates precoated with silica gel 60 F_{254}, layer thickness 0.2mm. Tetrakis(triphenylphosphine) palladium(0) was prepared according to the method of Coulson[10b] in 94% yield, m.p. 113-115°C (dec.) (lit.[10b] 116°). Cuprous bromide dimethylsulphide complex was prepared by the method of Keller *et al*[15] in 87% yield, m.p. 123-129°C (dec.) (lit.[15] 124-129°C). *E*-Methyl 4-bromo-2-butenoate was prepared by the method of Gedye *et al*[16] in 77% yield, b.p. 80-84°C/7mm Hg (lit.[16] 56-57°C/8.5 mmHg). 1-Bromo-5,5-dimethylcyclohexen-3-one was prepared by the method of Gruber *et al*[17], b.p. 61 - 64°C/1.8 mmHg (lit.[17] 53-55°C/1 mmHg). *E*-Methyl-3-bromo-2-propenoate was prepared by the method of Holy[18], b.p. 58-60°C/11 mmHg (lit.[18] 60°C/11 mmHg).

1-Tri-isopropylsilylindole (4). n-Butyl lithium (30 mmol) was added to a solution of indole (2.93g, 25 mmol) in THF (70 ml) at -20°C. After 1 h. a solution of chlorotri-isopropylsilane (5.78g, 30 mmol) in THF (20 ml) was added and the reaction stirred at -20°C for a further hour before allowing to warm to room temperature. The solution was concentrated to *ca.* 30 ml and was washed with water (2 x 50 ml). The aqueous layers were extracted with ether (2 x 25 ml) and the combined organic phases dried and concentrated. The product was purified by flash chromatography (petrol) to give the *title compound* (4) (6.85 g, 100%) as a colourless oil. Further purification by distillation (b.p. 140°C/0.2 mmHg), or preparative tlc, gave analytically pure material. (Found: C, 74.36; H, 10.05; N, 5.15. $C_{17}H_{27}NSi$ requires C, 74.66; H, 9.95; N, 5.12%); $\nu_{max.}$ ($CHCl_3$) 2940, 2840, 1520, 1450, 1270, 1140, 1015, 885, 740, 690 and 660 cm^{-1}; δ_H(90 MHz, $CDCl_3$) 1.1 {18H, d, *J* 8Hz, Si(CH*Me*$_2$)$_3$}, 1.4-2.0 {3H, m, Si(C*H*Me$_2$)$_3$}, 7.55 (1H, d, *J* 3Hz, 3-*H*) and 6.9-7.7 (5H, m, 2-, 4- and 7-*H*); *m/z* 273 (*M*+), 230 (100%), 202, 188, 174 and 160.

3-Methoxymethyl-1-tri-isopropylsilylindole (5). 3-Methoxymethylindole[19] (3.50 g, 22 mmol) was dissolved in THF (250 ml), n-butyl lithium (22.4 mmol) was added at -78°C and the reaction stirred for 1 h. Chlorotri-isopropylsilane (4.8 ml, 27 mmol) was added and the reaction stirred for a further hour at -78°C. Aqueous ammonium chloride (15% w/v, 100 ml) was added and the aqueous phase extracted with ether (2 x 200 ml). The combined organic extracts were dried, concentrated and purified by flash chromatography (petrol) to give the *indole* (5) as a colourless oil (6.80 g, 98%); $\nu_{max.}$ (film) 2948, 2868, 1611, 1078, 1016, 996, 923, 884, 775, 741, 691, 665 and 648 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0-1.3 {18H, m, Si(CH*Me*$_2$)$_3$}, 1.6 {3H, sept., *J* 7.5 Hz, Si(C*H*Me$_2$)$_3$}, 3.35 (3H, s, O*Me*), 4.12 (2H, s, CH_2OMe), 7.0-7.2 (3H, m, Ar*H*) and 7.35 (2H, m, Ar*H*); *m/z* 317 (*M*+). (Found: 317.2164. $C_{19}H_{31}NOSi$ requires 317.2175).

General procedure for the preparation of the indole complexes. - The indole (1.1 equiv.) and hexacarbonylchromium (1.0 equiv.) in a deoxygenated mixture of di-n-butyl ether (80 ml) and THF (5 ml) was heated under reflux in a Strohmeier apparatus[20] for 15 h. After cooling, the resultant orange solution was filtered through Celite with THF and concentrated under reduced pressure. Flash chromatography (petrol - ether; 80 : 20) and recrystallisation (petrol - dichloromethane) gave the indole complexes. So prepared were:-

Tricarbonyl(η^6*-1-tri-isopropylsilylindole)chromium(0)* (6) - as yellow needles (87%), m.p.137-139°C (dec.).(Found: C, 58.85; H, 6.69; N, 3.43. $C_{20}H_{27}CrNO_3Si$ requires C, 58.65; H, 6.65; N, 3.42%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1955, 1860, 1430, 1270, 1140, 1105, 880 and 630 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.2 {18H, d, *J* 7.5 Hz, Si(CH*Me*$_2$)$_3$}, 1.7 {3H, m, Si(C*H*Me$_2$)$_3$}, 5.15 (1H, t, *J* 6 Hz, 6-*H*), 5.3 (1H, t, *J* 6 Hz, 5-*H*), 6.25 (2H, d, *J* 6 Hz, 4- and 7-*H*), 6.45 (1H, d, *J* 4 Hz, 3-*H*) and 7.3 (1H, d, *J* 4 Hz, 2-*H*); *m/z* 409 (*M*+), 325, 273 and 230 (100%).

η^6*-(3-Methoxymethyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (7) - as yellow needles (72%), m.p.140-142°C (dec.). (Found: C, 58.20; H, 6.94; N; 3.12. $C_{22}H_{31}CrNO_4Si$ requires C, 58.26; H, 6.89; N, 3.09%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1950, 1860, 1430, 1270, 1140, 1105 and 1075 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.2 {18H, d, *J* 7 Hz, Si(CH*Me*$_2$)$_3$}, 1.7 {3H, m, Si(C*H*Me$_2$)$_3$}, 3.35 (3H, s, O*Me*), 4.5 (2H, br s, CH_2OMe), 5.05 (1H, t, *J* 6 Hz, 6-*H*), 5.3 (1H, dt, *J* 6, 1 Hz, 5-*H*), 6.15 (1H, d, *J* 6 Hz, 4-*H*); 6.25 (1H, dd, *J* 6, 1 Hz, 7-*H*) and 7.1 (1H, s, 2-*H*); *m/z* 453 (*M*+).

General Procedure for the Preparation of 4- Substituted Indole Complexes. - n-Butyl lithium (2mmol) was added to a solution of tricarbonyl-1-(tri-isopropylsilylindole)chromium(0) (1 mmol) in THF (50 ml) and TMEDA (1 ml) at -78°C. After 3 hours a solution of dry, purified electrophile (1.1 mmol) in THF (10 ml) was added and allowed to react at -78°C (15 - 30 min) before being warmed to room temperature. Aqueous ammonium chloride (15% w/v, 10 ml) was added and the organic layer was washed with water (3 x 25 ml). The aqueous layers were extracted with ether (2 x 25 ml) and the organic phases combined, dried,

concentrated and purified to give the 4- substituted indole complexes (8). So prepared (Table 1) were:-

η^6-*(4-Ethoxycarbonyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (8, R = CO_2Et). Electrophile: ethyl chloroformate; product purified by flash chromatography (petrol - dichloromethane; 8 : 2) and recrystallisation (petrol - THF - ether) to give orange - red crystals (60%), m.p. 134-136°C. (Found: C, 57.41; H, 6.49; N, 2.89. $C_{23}H_{31}CrNO_5Si$ requires C, 57.36; H, 6.49; N, 2.91%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1960, 1880, 1705, 1280, 1150, 1090 and 1010 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, $Si(CHMe_2)_3$}, 1.5 (3H, t, *J* 7 Hz, $CO_2CH_2CH_3$), 4.4 (2H, q, *J* 7 Hz, $CO_2CH_2CH_3$), 5.05 (1H, t, *J* 6 Hz, 6-*H*), 5.95 (1H, d, *J* 6 Hz, 5-*H*), 6.4 (1H, d, *J* 6 Hz, 7-*H*), 7.0 (1H, d, *J* 3 Hz, 3-*H*) and 7.35 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 481 (M^+), 397 (100%), 345, 326 and 302.

Tricarbonyl-(η^6*-1-tri-isopropylsilyl-4-trimethylsilylindole)chromium(0)* (8, R = $SiMe_3$). Electrophile: chlorotrimethylsilane; product purified by flash chromatography (petrol - dichloromethane; 9 : 1 to 7 : 3) and recrystallisation (petrol - ether) to give orange crystals (56%), m.p. 145°C (dec.). (Found: C, 57.63; H, 7.36; N, 2.92. $C_{23}H_{35}CrNO_3Si_2$ requires C, 57.34; H, 7.32; N, 2.91%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1950, 1865, 1370, 1135, 840 and 625 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 0.45 (9H, s, $SiMe_3$), 1.0 - 2.0 {21H, m, $Si(CHMe_2)_3$}, 4.8 - 5.3 (2H, m, 5-*H* and 6-*H*), 6.4 (2H, m, 3-*H* and 7-*H*) and 7.35 (1H, d, *J* 4 Hz, 2-*H*); *m/z* 481 (M^+), 425, 397, 345 (100%), 302 and 238.

η^6-*(4-Methoxycarbonyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (8, R = CO_2Me). Electrophile: methyl chloroformate; product purified by flash chromatography (petrol - dichloromethane; 85 : 15 to 70 : 30) and recrystallisation (petrol - ether) to give red crystals (59%), m.p. 100 - 101°C. (Found: C, 56.74; H, 6.33; N, 2.96. $C_{22}H_{29}CrNO_5Si$ requires C, 56.61; H, 6.25; N, 3.00%); $\nu_{max.}$ ($CHCl_3$) 2940, 2870, 1960, 1880, 1710, 1420, 1285, 1190, 1150, 1095 and 1015 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, $Si(CHMe_2)_3$}, 4.0 (3H, s, CO_2Me), 5.1 (1H, t, *J* 6 Hz, 6-*H*), 6.0 (1H, d, *J* 6 Hz, 5-*H*), 6.5 (1H, d, *J* 6 Hz, 7-*H*), 7.1 (1H, d, *J* 3 Hz, 3-*H*) and 7.45 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 467 (M^+), 411, 383 (100%), 331 and 288.

η^6-*[4-(3-Methylbut-2-enyl)-1-tri-isopropylsilylindole]tricarbonylchromium(0)* (8, R = $CH_2CH{=}CMe_2$). Electrophile: 3-methylbut-2-enyl bromide; product purified by flash chromatography (petrol - dichloromethane; 95 : 5 to 80 : 20) and recrystallisation (petrol - ether) to give orange crystals (36%), m.p. 112-113.5°C. (Found: C, 63.19; H, 7.44; N, 2.94. $C_{25}H_{35}CrNO_3Si$ requires C, 62.87; H, 7.39; N, 2.93%); $\nu_{max.}$($CHCl_3$) 2930,2 880, 1945, 1860, 1445, 1420, 1270, 1145, 1105 and 1010 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, $Si(CHMe_2)_3$}, 1.8 (6H, s, $CH_2CH{=}CMe_2$), 3.6 (2H, br d, *J* 8 Hz, $CH_2CH{=}CMe_2$), 4.9 - 5.4 (3H, m, 5-*H*, 6-*H* and $CH_2CH{=}CMe_2$), 6.1(1H, d, *J* 6 Hz, 7-*H*), 6.45(1H, d, *J* 4 Hz, 3-*H*) and 7.25 (1H, d, *J* 4 Hz, 2-*H*); *m/z* 477 (M^+), 461, 393 and 341 (100%).

η^6-*(4-Iodo-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (8, R = I). Electrophile: iodine; product purified by flash chromatography (petrol - ether; 9 : 1) and recrystallisation (petrol) to give orange crystals (76%), m.p. 84 - 87°C. (Found: C, 44.90; H, 4.87; N, 2.59. $C_{20}H_{26}CrINO_3Si$ requires C, 44.87; H, 4.89; N, 2.62%); $\nu_{max.}$ ($CHCl_3$) 1960 and 1885 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.13 {9H, d, *J* 7.5 Hz, $Si(CHMe_2)_3$}, 1.21 {9H, d, *J* 7.5 Hz, $Si(CHMe_2)_3$}, 1.65 {3H, sept., *J* 7.5 Hz, $Si(CHMe_2)_3$}, 5.16 (1H, t, *J* 6.5 Hz, 6-*H*), 5.47 (1H, d, *J* 6.5 Hz, 5-*H*), 6.12 (1H, dd, *J* 6.5, 3.2 Hz, 7-*H*), 6.48 (1H, d, *J* 3.4 Hz, 3-*H*) and 7.31 (1H, d, *J* 3.4Hz, 2-*H*); *m/z* 535 (M^+), 479, 451 (100%), 408, 399 and 356.

Tricarbonyl (η^6*-1-tri-isopropylsilyl-4-trimethylstannylindole)chromium(0)* (8, R = $SnMe_3$). Electrophile: chlorotrimethylstannane; product purified by flash chromatography (petrol - ether; 95 : 5) and recrystallisation (petrol - chloroform) to give yellow - orange crystals (69%), m.p. 133-135°C. (Found: C, 48.13; H, 6.16; N, 2.56. $C_{23}H_{35}CrNO_3SiSn$ requires C, 48.27; H, 6.16; N, 2.45%); $\nu_{max.}$ (Nujol) 2937, 2861, 1935, 1864, 1832, 1465, 1378 and 1153 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.51 (9H, s, $SnMe_3$), 1.1 - 1.25 {18H, m, $Si(CHMe_2)_3$}, 1.68 {3H, sept., *J* 7 Hz, $Si(CHMe_2)_3$}, 5.10 (1H, t, *J* 6 Hz, 6-*H*), 5.17 (1H, d, *J* 6 Hz, 5-*H*), 6.31 (1H, d, *J* 3 Hz, 3-*H*), 6.36 (1H, d, *J* 6 Hz, 7-*H*) and 7.35 (1H, d, *J* 3Hz, 2-H); *m/z* 573 (M^+), 517, 489 (100%), 437, 422 and 273.

η^6-*(4-Methoxycarbonyl-3-methoxymethyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (9, R = CO_2Me). Electrophile: methyl chloroformate; product purified by flash chromatography (petrol - dichloromethane; 8 : 2 to 1 : 1) and recrystallisation (petrol - dichloromethane) to give orange - red crystals (61%), m.p. 147-149°C (dec.). (Found: C, 56.21; H, 6.20; N, 2.73. $C_{24}H_{33}CrNO_6Si$ requires C, 56.32; H, 6.43; N, 2.74%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1960, 1880, 1705, 1280, 1150, 1090, 1065 and 1010 cm^{-1}; δ_H (90 MHz,

$CDCl_3$) 1.0 - 2.0 {21H, m, Si(C*H*Me_2)$_3$}, 3.45 (3H, s, CH_2O*Me*), 4.0 (3H, s, CO_2*Me*), 4.7 (1H, d, *J* 16 Hz, C*H*$_A$H$_B$OMe), 4.9 (1H, d, *J* 16 Hz, CH$_A$*H*$_B$OMe), 5.1 (1H, t, *J* 6 Hz, 6-*H*), 6.0 (1H, d, *J* 6 Hz, 5-*H*), 6.5 (1H, d, *J* 6 Hz, 7-*H*) and 7.2 (1H, s, 2-*H*); *m/z* 511 (*M*$^+$).

η^6-*(3-Methoxymethyl-1-tri-isopropylsilyl-4-trimethylsilylindole)tricarbonylchromium(0)* (**9**, R = $SiMe_3$). Electrophile: chlorotrimethylsilane; product purified by flash chromatography (petrol - ether; 9 : 1) and recrystallisation to give orange crystals (81%), m.p. 132 - 134°C. (Found: C, 56.91; H, 7.55; N, 2.59. $C_{25}H_{39}CrNO_4Si_2$ requires C, 57.11; H, 7.48; N, 2.66%); $\nu_{max.}$ (Nujol) 2963, 2872, 1941, 1864, 1837, 1408 and 1366 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.55 (9H, s, Si*Me*$_3$), 1.1 - 1.3 {18H, m, Si(CH*Me*$_2$)$_3$}, 1.7 {3H, sept., *J* 7 Hz, Si(C*H*Me_2)$_3$}, 3.40 (3H, s, O*Me*), 4.5 (1H, dd, *J* 12, 1 Hz, C*H*$_A$H$_B$OMe), 4.65 (1H, dd, *J* 12, 1 Hz, CH$_A$*H*$_B$OMe), 4.95 (1H, dd, *J* 7, 6 Hz, 6-*H*), 5.37 (1H, dd, *J* 6, 1 Hz, 5-*H*), 6.45 (1H, dd, *J* 7, 1 Hz, 7-*H*) and 7.45 (1H, s, 2-*H*); *m/z* 525 (*M*$^+$), 389, 317.

η^6-*(3-Methoxymethyl-1-tri-isopropylsilyl-4-trimethylstannylindole)tricarbonylchromium(0)* (**9**, R = $SnMe_3$). Electrophile: chlorotrimethylstannane; product purified by flash chromatography (petrol - ether; 9 : 1) and recrystallisation (petrol) to give yellow crystals (79%), m.p. 142 - 143°C. (Found: C, 48.82; H, 6.35; N, 2.30. $C_{25}H_{39}CrNO_4SiSn$ requires C, 48.72; H, 6.38; N, 2.27%); $\nu_{max.}$ (Nujol) 2950, 2871, 1941, 1851, 1462, 1399, 1372, 1152, 1090 and 1075 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.40 (9H, s, Sn*Me*$_3$), 1.1 - 1.25 {18H, m, Si(CH*Me*$_2$)$_3$}, 1.68 {3H, sept., *J* 6.25 Hz, Si(C*H*Me_2)$_3$}, 3.35 (3H, s, O*Me*), 4.31 (1H, d, *J* 13 Hz, C*H*$_A$H$_B$OMe), 4.70 (1H, d, *J* 13 Hz, CH$_A$*H*$_B$OMe), 5.13 (1H, t, *J* 6 Hz, 6-*H*), 5.18 (1H, dd, *J* 6, 1 Hz, 5-*H*), 6.37 (1H, dd, *J* 6, 1 Hz, 7-*H*) and 7.25 (1H, s, 2-*H*); *m/z* 617 (*M*$^+$), 533, 518, 503, 487, 436.

η^6-*(4-Iodo-3-methoxymethyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (**9**, R = I). Electrophile: iodine; product purified by flash chromatography (petrol - ether; 9 : 1) and recrystallisation (petrol) to give orange crystals (66%), m.p. 57 -60°C. (Found: C, 45.80; H, 5.47; N, 2.18. $C_{22}H_{30}CrINO_4Si$ requires C, 45.60; H, 5.22; N, 2.42%); $\nu_{max.}$ (neat) 2951, 2871, 1950, 1860, 1585, 1465, 1435, 1305, 1202, 1143, 1114, 1089, 1074, 968, 953, 883, 675 and 633 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.0 - 1.3 {18H, m, Si(CH*Me*$_2$)$_3$}; 1.62 {3H, sept.,*J* 7.5 Hz, Si(C*H*Me_2)$_3$}, 3.45 (3H, s, O*Me*), 4.58 (1H, d, *J* 12.5 Hz, C*H*$_A$H$_B$OMe), 4.74 (1H, d, *J* 12.5 Hz, CH$_A$*H*$_B$OMe), 5.15 (1H, t, *J* 6.5 Hz, 6-*H*), 5.5 (1H, d, *J* 6.5 Hz, 5-*H*), 6.1 (1H, d, *J* 6.5 Hz, 7-*H*) and 7.25 (1H, s, 2-*H*); *m/z* 579 (*M*$^+$), 495, 465 and 443.

General procedure for the preparation and use of the complexed indole copper reagents. - A solution of lithiated indole complex (1 mmol) was added to a suspension of copper(I) bromide-dimethyl sulphide complex (2 mmol) in THF (10 ml) at -23°C. After 30 min. a solution of the electrophile (1.1 mmol) in THF (10 ml) was added and allowed to react for 3 h. at room temperature. Aqueous ammonium chloride (15% w/v, 25 ml) and methanol (25 ml) were added and the resulting gelatinous suspension filtered through Celite, eluting with THF. The organic layer was washed with water (2 x 25 ml) and the aqueous layers extracted with ether (2 x 25 ml). The combined organic extracts were dried and concentrated and purified to give the 4- substituted indole complexes (**8**). So prepared (Table 2) were:-

η^6-*(4-Acetyl-1-tri-isopropylsilylindole)tricarbonylchromium(0)* (**8**, R = COMe). Electrophile: acetyl chloride; product purified by flash chromatography (petrol - dichloromethane, 8 : 2 to 0 : 10) and recrystallisation (petrol - dichloromethane) to give red needles (45%), m.p. 142-145°C (dec.). (Found: C 58.71; H, 6.62; N, 3.25. $C_{22}H_{29}CrNO_4Si$ requires C, 58.46; H, 6.47; N, 3.10%); $\nu_{max.}$ ($CHCl_3$) 2950, 2870, 1960, 1880, 1670, 1515, 1410, 1360 and 1255 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0- 2.0 {21H, m, Si(C*HMe*$_2$)$_3$}, 2.4 (3H, s, CO*Me*), 5.1 (1H, t, *J* 6 Hz, 6-*H*), 6.0 (1H, d, *J* 6 Hz, 5-*H*), 6.5 (1H, d, *J* 6 Hz, 7-*H*), 7.1 (1H, br d, *J* 3 Hz, 3-*H*) and 7.4 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 452 (*M*$^+$).

η^6-*[4-(3-Methylbut-2-enyl)-1-tri-isopropylsilylindole] tricarbonylchromium(0)* (**8**, R = CH_2CH=CMe_2). Electrophile: 3-methylbut-2-enyl bromide; product purified by flash chromatography (petrol - dichloromethane; 95 : 5 to 80 : 20) and recrystallisation (petrol - ether) to give the title compound (51%) which was identical to that obtained directly from the 4- lithio species.

η^6-*[4-(E-3-Methyoxycarbonylprop-2-enyl)-1-tri-isopropylsilylindole]tricarbonylchromium(0)* (**8**, R = CH_2CH=$CHCO_2$Me). Electrophile: methyl *E*-4-bromobut-2-enoate; product purified by flash chromatography (petrol - ether 99 : 1 to 1 : 1) and recrystallisation (petrol) to give yellow needles (58%), m.p. 129-132°C. (Found: C, 58.90; H, 6.58; N, 2.80. $C_{25}H_{33}CrNO_5Si$ requires C, 59.15; H, 6.55; N, 2.76%); $\nu_{max.}$ ($CHCl_3$) 3400, 2980, 1960, 1880, 1730 and 1420 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.0 - 1.4 {18H, m, Si(CH*Me*$_2$)$_3$}, 1.5 - 1.8 {3H,

m, Si(C*H*Me$_2$)$_3$}, 3.7 (3H, s, CO_2*Me*), 3.95 (2H, d, *J* 7 Hz, CH_2CH=CHCO$_2$Me), 4.95 (1H, d, *J* 7 Hz, 5-*H*): 5.34 (1H, t, *J* 7 Hz, 6-*H*), 5.9 (1H, d, *J* 14 Hz, CH=C*H*CO$_2$Me), 6.15 (1H, d, *J* 7 Hz, 7-*H*), 6.4 - 6.5 (1H, m, 3-*H*), 7.15 (1H, dt, *J* 14, 7 Hz, CH$_2$C*H*=CHCO$_2$Me) and 7.25 - 7.3 (1H, m, 2-*H*); *m/z* 371 (*M*$^+$, 100%), 328 and 296.

General procedure for the palladium catalysed cross coupling reaction. The complexed indole copper reagent was prepared as described above and reacted with a solution of the electrophile (1.1mmol) in THF (10ml) in the presence of tetrakis(triphenylphosphine)palladium(0) (4mol%) for 3 h. The reaction was worked up as described below to give the 4- substituted indole complexes. So prepared were:-

η^6-*(4-Ethenyl-1-tri-isopropylsilylindole)tricarbonyl chromium(0)* (**8**, R = CH=CH$_2$). Electrophile: vinyl bromide; product purified by flash chromatography (petrol - dichloromethane, 90 : 10 to 75 : 25) to give red needles (43%), m.p. 121-123°C. (Found: C, 60.66; H, 6.67; N, 3.24. $C_{22}H_{29}CrNO_3Si$ requires C, 60.67; H, 6.71; N, 3.22%); $\nu_{max.}$ ($CHCl_3$) 2950, 1965, 1880, 1605, 1595, 1470, 1430 and 1120 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, Si(C*HMe*$_2$)$_3$}, 5.0 (1H, dd, *J* 6, 1 Hz, CH=CHH_{cis}), 5.1 (1H, d, *J* 6 Hz, 5-*H*), 5.3 (1H, dd, *J* 16, 1 Hz, CH=CHH_{trans}), 5.4 (1H, t, *J* 6 Hz, 6-*H*), 6.3 (1H, d, *J* 6 Hz, 7-*H*), 6.8 (1H, dd, *J* 16, 6 Hz, C*H*=CH$_2$), 7.0 (1H, d, *J* 3 Hz, 3-*H*) and 7.3 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 436 (*M*$^+$).

η^6-*[4-(5,5-Dimethyl-3-oxocyclohexen-1-yl)-1-tri-isopropylsilylindole]tricarbonylchromium(0)* (**8**, R = -C=CHCOCH$_2$CMe$_2$CH$_2$). Electrophile: 1-chloro-5,5-dimethyl-3-oxocyclohexene; product purified by flash chromatography (petrol - dichloromethane 8 : 2 to 4 : 6) and recrystallisation (petrol - dichloromethane) to give deep red crystals (34%), m.p. 192-194°C (dec.). (Found: C, 62.97; H, 6.85; N, 2.94. $C_{28}H_{37}CrNO_4Si$ requires C, 63.20; H, 7.01; N, 2.63%); $\nu_{max.}$ ($CHCl_3$) 2935, 1960, 1880, 1635, 1595, 1440, 1400 and 1125 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 0.9 - 2.0 {27H, m, Si(C*HMe*$_2$)$_3$ and C*Me*$_2$}, 2.3 (2H, s, CH_2CO-), 2.45 (2H, s, CH_2C=CH-), 5.1 (1H, t, *J* 6 Hz, 6-*H*), 6.0 (1H, d, *J* 6 Hz, 5-*H*), 6.3 (1H, s, C=C*H*-), 6.5 (1H, d, *J* 6 Hz, 7-*H*), 7.1 (1H, d, *J* 3 Hz, 3-*H*) and 7.4 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 532 (*M*$^+$).

η^6-*[4-(E-2-Methoxycarbonylethenyl)-1-tri-isopropylsilylindole]tricarbonylchromium(0)* (**8**, R = CH=CHCO$_2$Me). Electrophile: methyl *E*-3-bromopropenoate; product purified by flash chromatography (petrol - dichloromethane 9 : 1 to 4 : 6) and recrystallisation (petrol - dichloromethane) to give red crystals (41%), m.p. 162-164°C (dec.). (Found: C, 58.21; H, 6.47; N, 2.80. $C_{24}H_{31}CrNO_5Si$ requires C, 58.40; H, 6.33; N, 2.84%); $\nu_{max.}$ ($CHCl_3$) 2940, 1960, 1895, 1710, 1605, 1460, 1430, 1195 and 1110 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, Si(C*HMe*$_2$)$_3$}, 3.8 (3H, s, CO_2*Me*), 5.3 (1H, t, *J* 6 Hz, 6-*H*), 5.6 (1H, d, *J* 6 Hz, 5-*H*), 6.2 (1H, d, *J* 15 Hz, CH=C*H*CO$_2$Me), 6.4 (1H, d, *J* 6 Hz, 7-*H*), 7.0 (1H, d, *J* 3 Hz, 3-*H*), 7.1 (1H, d, *J* 15 Hz, C*H*=CHCO$_2$Me) and 7.3 (1H, d, *J* 3 Hz, 2-*H*); *m/z* 493 (*M*$^+$).

General procedure for the photolytic decomplexation of the indole complexes. - A dilute solution of the complex in acetonitrile (*ca.* 300 mg in 150 ml) was irradiated with a tungsten lamp in air for 2 - 24 hours until t.l.c. indicated that reaction had gone to completion. Filtration through Celite and removal of the solvent gave the indoles which were further purified as described below.

General procedure for the decomplexation of the indole complexes via the action of refluxing pyridine. - A deoxygenated solution of the indole complex in pyridine(*ca* .100 mg in 1 ml) was heated under reflux, under a nitrogen atmosphere for 2 h. Removal of the excess pyridine under reduced pressure and flash chromatography gave the free indole and (pyridine)$_3$Cr(CO)$_3$.

So prepared by the method indicated were;-

4-Ethoxycarbonyl-1-tri-isopropylsilylindole (**10**, R = CO_2Et). Photolytic cleavage: product purified by preparative t.l.c. [eluant: petrol (b.p. 30-40°C) - ether 1:1) to give a clear oil (84%). (Found: C, 69.47; H, 9.04; N, 4.24. $C_{20}H_{31}O_2NSi$ requires C, 69.52; H, 9.04; N, 4.05%); $\nu_{max.}$ ($CHCl_3$) 2940, 2870, 1690, 1440, 1280, 1150, 1095 and 1015 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.15 {18H, d, *J* 7Hz, Si(CH*Me*$_2$)$_3$}, 1.47 (3H, t, *J* 7 Hz, CO_2CH_2*Me*), 1.72 {3H, sept., *J* 7 Hz, Si(C*H*Me$_2$)$_3$}, 4.46 (2H, q, *J* 7 Hz, CO_2CH_2Me), 7.2 (1H, t, *J* 6 Hz, 6-*H*), 7.33 (1H, dd, *J* 3, 0.8 Hz, 3-*H*), 7.4 (1H, d, *J* 3 Hz, 2-*H*), 7.71 (1H, dt, *J* 7, 0.8 Hz, 7-*H*) and 7.93 (1H, dd, *J* 7, 0.8 Hz, 5-*H*); *m/z* 345 (*M*$^+$), 302 (100%), 274 and 256.

1-Tri-isopropylsilyl-4-trimethylsilylindole (**10**, R = SiMe$_3$). Photolytic cleavage: product purified by preparative t.l.c. [petrol (b.p. 30-40°C) - ether 95 : 5] to give a colourless oil (93%). (Found: C, 69.21; H, 10.15; N, 3.89. $C_{20}H_{35}NSi_2$ requires C, 69.49; H, 10.21; N, 4.05%); ν_{max} ($CHCl_3$) 2920, 2870, 1395, 1275, 1145, 1020 and 830 cm^{-1}; δ_H (250 Mz, $CDCl_3$) 0.4 (9H, s, Si*Me*$_3$), 1.15 {18H, d, *J* 7 Hz, Si(CH*Me*$_2$)$_3$}, 1.7 {3H, m,

$Si(CHMe_2)_3$}, 6.75 (1H, dd, *J* 3, 0.8 Hz, 3-*H*), 7.13 (1H, t, *J* 6 Hz, 6-*H*), 7.25 - 7.3 (2H, m, 2-*H* and 5-*H*) and 7.54 (1H, dt, *J* 6, 0.8 Hz, 7-*H*); *m/z* 345 (*M*+, 100%), 330 and 302.

1-Tri-isopropylsilyl-4-trimethylstannylindole (**10**, R = $SnMe_3$). Photolytic cleavage: crude product (which was unstable to column chromatography) isolated as a colourless oil (90%); $\nu_{max.}$ (neat) 2948, 2869, 1608, 1514, 1450, 1403, 1369, 1273, 1142, 1074, 1016, 997, 979, 884, 742, 720, 690, 662, 588, 570 and 518 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 0.3 (4H, s, $SnMe_3$), 0.4 (5H, s, $SnMe_3$), 1.15 {18H, d, *J* 7.5 Hz, $Si(CHMe_2)_3$}, 1.6 (3H, sept., *J* 7.5 Hz, $Si(CHMe_2)_3$}, 6.55-6.65 (1H, m, 3-*H*), 7.0-7.3 (2H, m, 5- and 6-*H*) and 7.4-7.75 (2H, m, 2- and 7-*H*); *m/z* 437 (*M*+), 422, 392, 273 and 230 (100%); (Found: *M*+, 437.1565. $C_{20}H_{35}NSiSn$ requires 437.1561).

4-(E-2-Methoxycarbonylethenyl)-1-tri-isopropylsilylindole (**10**, R = $CH{=}CHCO_2Me$). Photolytic cleavage: product isolated as a yellow oil (97%). $\nu_{max.}$ (neat) 2960, 1715, 1610, 1595, 1460, 1420, 1205 and 1110 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 1.0 - 2.0 {21H, m, $Si(CHMe_2)_3$}, 3.75 (3H, s, CO_2Me), 6.1 (1H, d, *J* 15 Hz, $CH{=}CHCO_2Me$) and 7.1 - 7.8 (6H, m, 5 Ar*H* and $CH{=}CHCO_2Me$); *m/z* 357 (*M*+); (Found: 357.2138. $C_{21}H_{31}NO_2Si$ requires 357.2124).

3-Methoxymethyl-1-tri-isopropylsilyl-4-trimethylsilylindole (**11**, R = $SiMe_3$). Photolytic cleavage: product purified by flash chromatography (petrol) to give a colourless oil (92%); $\nu_{max.}$ (neat) 2949, 2869, 1586, 1551, 1465, 1396, 1304, 1251, 1169, 1145, 1103, 1080, 1018, 883, 863 and 838 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.45 (9H, s, $SiMe_3$), 1.25 {18H, d, *J* 7.5 Hz, $Si(CHMe_2)_3$}, 2.72 {3H, sept., *J* 7.5 Hz, $Si(CHMe_2)_3$}, 3.45 (3H, s, O*Me*), 4.75 (2H, s, CH_2OMe), 7.12 (1H, t, *J* 7.5 Hz, 6-*H*), 7.3-7.45 (2H, m, 2- and 5-*H*) and 7.55 (1H, dd, *J* 7.5, 1 Hz, 7-*H*); *m/z* 389 (*M*+, 100%), 374 and 358. (Found: *M*+, 389.2563; $C_{22}H_{39}NOSi_2$ requires 389.2570).

3-Methoxymethyl-1-tri-isopropylsilyl-4-trimethylstannylindole (**11**, R = $SnMe_3$). Photolytic cleavage; product (which was not stable to chromatography) isolated as a colourless oil (90%); $\nu_{max.}$ (neat) 2948, 2869, 1451, 1401, 1307, 1159, 1133, 1100, 1078, 1017, 996, 979, 962, 884, 760, 742, 691, 666, 648, 579 and 519 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 0.50 (9H, s, $SnMe_3$); 1.2 {18H, d, *J* 7 Hz, $Si(CHMe_2)_3$}, 1.7 {3H, sept., *J* 7 Hz, $Si(CHMe_2)_3$}, 3.4 (3H, s, O*Me*), 4.75 (2H, s, CH_2OMe) and 7.1-7.7 (4H, m, Ar*H*); *m/z* 481 (*M*+), 466, 436, 317 (100%), 286 and 274. (Found: *M*+, 481.1813. $C_{22}H_{39}NOSiSn$ requires 481.1823).

4-Iodo-3-methoxymethyl-1-tri-isopropylsilylindole (**11**, R = I). Photolytic cleavage: Product isolated as a colourless oil (94%); $\nu_{max.}$ (neat) 2948, 2868, 1596, 1543, 1466, 1413, 1385, 1308, 1254, 1193, 1167, 1138, 1103, 1083, 1017, 964 and 884 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.15 {18H, d, *J* 7.5 Hz, $Si(CHMe_2)_3$}, 1.67 {3H, sept., *J* 7.5 Hz, $Si(CHMe_2)_3$}, 3.47 (3H, s, O*Me*), 4.78 (2H, s, CH_2OMe), 6.8 (1H, t, *J* 7.5 Hz, 6-*H*), 7.3 (1H, s, 2-*H*), 7.45 (1H, d, *J* 7.5 Hz, 5-*H*) and 7.6 (1H, d, *J* 7.5 Hz, 7-*H*); *m/z* 443 (*M*+), 412 and 317 (100%). (Found: *M*+, 443.1146; $C_{19}H_{30}INOSi$ requires 443.1141).

General procedure for the fluoride induced desilylation of the N*-protected 4-substituted indoles.* Tetrabutylammonium fluoride (1.0 M solution in THF, 0.6 - 1.0 mmol) was added to a solution of the 4-substituted-1-tri-isopropylsilylindole either in complexed or uncomplexed form (0.3 - 0.5 mmol) in THF (5 ml) at 0°C. When t.l.c. analysis indicated that reaction was complete, dichloromethane (10 ml) was added and the reaction mixture washed with water (3 x 10 ml). The combined aqueous layers were back-extracted with dichloromethane (10 ml) and the combined organic layers dried and concentrated and purified. Additionally, products still complexed were decomplexed as indicated to give the 4- substituted indoles. So prepared were:-

4-Ethoxycarbonylindole (**12**, R = CO_2Et). - From the uncomplexed arene (**10**, R = CO_2Et): purified by flash chromatography (petrol - dichloromethane 9 : 1 to 1 : 1) and recrystallisation (ethanol - petrol) to give white crystals (100%), m.p. 70-71°C (lit.[21] 70-71°C).

4-Trimethylsilylindole(**12**, R = $SiMe_3$). - From the complex (**8**, R = $SiMe_3$) followed by thermal decomplexation with pyridine: purified by flash chromatography (petrol - ether 9 : 1 to 1 : 1) and recrystallisation (petrol) as white crystals (86%), m.p. 65 - 66°C (lit.[22] 63.5 - 64°C).

4-Methoxycarbonylindole (**12**, R = CO_2Me). - From the complex (**8**, R = CO_2Me) with subsequent thermal decomplexation with pyridine: purified by flash chromatography (petrol - dichloromethane 10 : 0 to 0 : 10) and recrystallisation (methanol - petrol), as white crystals (81%), m.p.68 -69°C (lit.[21,23] 64°C, 67-69°C).

4-Phenylthioindole (**12**, R = SPh). From the unstable complex (**8**, R = SPh) followed by photolytic

decomplexation: purified by flash chromatography (petrol - ether 85 : 15 to 70 : 30) and preparative t.l.c. [petrol (b.p. 30-40°C) - ether; 1 : 1] to give a yellow oil (26%). (Found: C, 74.52; H, 4.97; N, 6.18. $C_{14}H_{11}NS$ requires C, 74.63; H, 4.92; N, 6.22%); $\nu_{max.}$ ($CHCl_3$) 3 480, 1 580, 1410, 1330, 1190, 1135, 1100, 1070, 1030, 850 and 640 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 6.54 (1H, m, 3-*H*), 7.1 - 7.3 (8H, m, 2-, 5-, 6-*H* and *Ph*), 7.35 (1H, dt, *J* 7, 0.8 Hz, 7-*H*) and 8.1 - 8.3 (1H, br s, N*H*); *m/z* 225 (M^+, 100%).

4-(3-Methylbut-2-enyl)indole (**12**, R = $CH_2CH{=}CMe_2$). From the complex (**8**, R = $CH_2CH{=}CMe_2$) followed by photolytic decomplexation: purified by preparative t.l.c. [petroleum ether (bp 30-40°C) - ether 7 : 3] to give a clear oil (95%), spectroscopically identical to previously reported material[24].

REFERENCES

1. P.A. Stadler and P. Stutz in 'The Alkaloids', Ed. R.H.F. Manske, Academic Press, New York, 1975, p. 1.
2. M. Yamazaki in 'The Biosynthesis of Mycotoxins', Ed. P. Steyn, Academic Press, New York, 1980, p. 204.
3. K. Irie, N. Hagiwara and K. Koshimizu, *Tetrahedron*, 1987, **43**, 5251, and references there cited.
4. British Pharmacopoeia, HMSO, 1980, p. 175.
5. R. J. Sundberg, "The Chemistry of Indoles", Academic Press, New York, 1970; W. J. Houlihan. Ed., "Indoles" Part 1, Wiley Interscience, New York, 1972.
6. See R.A. Hollins, L.A. Colnago, V.M. Salim and M.C. Siedl, *J. Heterocyclic Chem.*, 1979, **16**, 993 and references there cited.
7. A. P. Kozikowski, *Heterocycles*, 1981, **16**, 267; D. C. Horwell, *Tetrahedron*, 1980, **36**, 3123.
8. M. F. Semmelhack, *Ann. N. Y. Acad. Sci.*, 1977, **295**, 32; G. Jaouen, *Ann. N. Y. Acad. Sci.*, 1977, **295**, 59.
9. G. Nechvatal and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1982, 467.
10. a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551; b) D. R. Coulson, *Inorg. Syntheses*, 1972, **13**, 121.
11. G. Jaouen and R. Dabard, *Tetrahedron Lett.*, 1971, 1015.
12. P. J. Beswick, S. J. Leach, N. F. Masters and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1984, 46.
13. G. H. Posner, "An Introduction to Synthesis using Organocopper Reagents", Wiley, New York, 1980. J. F. Normant, *Synthesis*, 1972, 63.
14. K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S-I. Komada, I. Nakajima, A. Minato and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1958.
15. R. N. Keller and H. D. Wycoff. *Inorg. Syntheses*, 1946, **2**, 1.
16. R. W. Gedye, K. C. Westway, P. Arora, R. Bisson and A. H. Khalil, *Canad. J. Chem.*, 1977, **55**, 1218.
17. L. Gruber, I. Tomoskozi and L. Radicz, *Synthesis*, 1975, 708.
18. A. Holy, *Collect. Czech. Chem. Commun.*, 1974, **39**, 3117.
19. T. A. Geissman and A. Armen, *J. Am. Chem. Soc.*, 1952, **74**, 3916.
20. W. Strohmeier, *Chem. Ber.*, 1961, **94**, 2490.
21. E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 1954, **37**, 1826.
22. A. G. M. Barrett, D. Dauzonne, I. A. O'Neil and A. Renaud, *J. Org. Chem.*, 1984, **49**, 4409.
23. G. S. Ponticello and J. J. Baldwin, *J. Org. Chem.*, 1979, **44**, 4003.
24. H. Pleininger, E. Meyer, F. Sharif-Nassirian and E. Weidman, *Liebigs Ann. Chem.*, 1976, 1475.