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Transition Metal Mediated Thiation of Aromatic Rings

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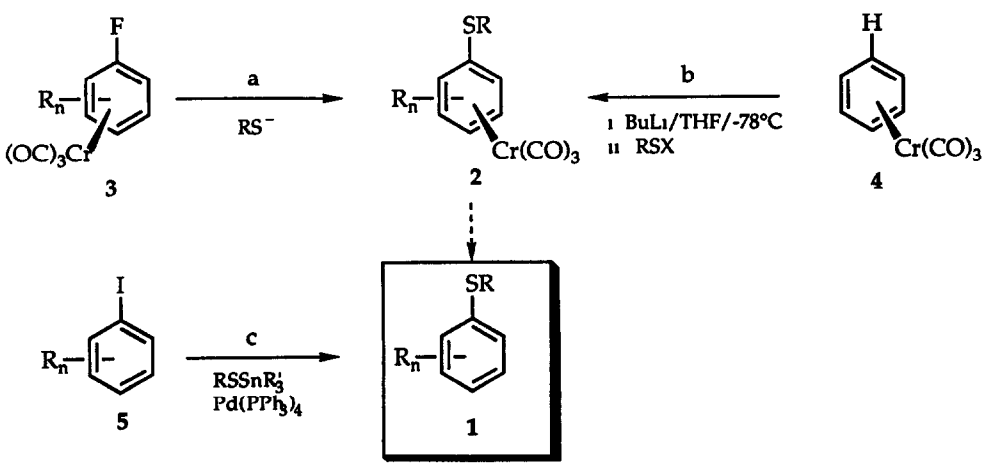
Abstract – Three approaches to aromatic thiation have been studied Dependent upon access to the necessary starting material, displacement of halogen in haloarenetricarbonylchromium(0) complexes by nucleophilic sulphur, quenching of lithiated arenetricarbonylchromium(0) complexes by electrophilic sulphur or palladium catalysed cross coupling of aryl iodides with alkylthiotrialkylstannanes were all effective and apparently general in scope The latter is the preferred process

Sulphur(II) functionalised aromatic systems are widespread in natural and commercial products[1] and the conventional formation of the aryl–sulphur bond by a variety of mechanistic types is widely reported[2] However these processes frequently involve fierce conditions (e g copper thiolates at high temperature[3]) or require unwanted activation (nitro-groups for nucleophilic substitution[2a]) and we have sought to develop mild methods usually operating at or below ambient temperature

Scheme 1



We report here three approaches to aryl–sulphur bond formation (Schemes 1a-c, 2) which rely on activation of the substrate by complexation with a tricarbonylchromium(0) unit and/or palladium catalysis. The routes are complementary, dependent upon the availability of the haloarenes (routes a, c) or of a specific lithiation process (route b) Route c could be operated with or without chromium complexation

The first approach (Scheme 1a) uses the electron withdrawing properties of the tricarbonylchromium unit to render an aromatic ring susceptible to nucleophilic displacement[4] We[5], and others[6] have reported the displacement of fluoride and other halides by sulphur nucleophiles, but few examples have been studied We therefore examined a range of thiolate displacements of fluoride in these complexes. The results are presented in Table 1

Table 1. Thiolate Displacement of Fluoride in Chromium Complexes (3)

Run	Complex (3)	Thiolate	Conditions	Yield(2), (%)
1	R_n = H	BuSNa	25°C/ 3h	74
2	R_n = H	*cyclo*-$C_6H_{11}SNa$	25°C/ 14h	55
3	R_n = H	CH_2=$CHCH_2SNa$	25°C/ 14h	72
4	R_n = H	PhSNa	67°C/ 6h	53
5	R_n = H	MeO_2CCH_2SNa	67°C/ 21h	60
6	R_n = H	$(EtO)_2CHCH_2SNa$	25°C/ 2h	99
7	R_n = H	$PhCH_2SNa$	0°C → r t	90
8	R_n = H, 'F' = I	$PhCH_2SNa$	25°C/ 14h	52
9	R_n= 2-Me	$PhCH_2SNa$	0°C → r t	72
10	R_n= 2-MeO	$PhCH_2SNa$	0°C → r t	90
11	R_n= 4-MeO	$PhCH_2SNa$	0°C → r t	83
12	R_n= 2-Me-4-MeO	$PhCH_2SNa$	0°C → r t	78
13	R_n= 2-MeO_2C	$PhCH_2SNa$	0°C → r t	67[a]
14	R_n= 2-MeO-6-Me	$PhCH_2SNa$	0°C → r t	78
15	R_n= 2-Me_3Si-4-MeO	$PhCH_2SNa$	0°C → r t	79[b]
16	R_n= 2-Me-5-MeO-6-Me_3Si	$PhCH_2SNa$	0°C → r t	78[b]

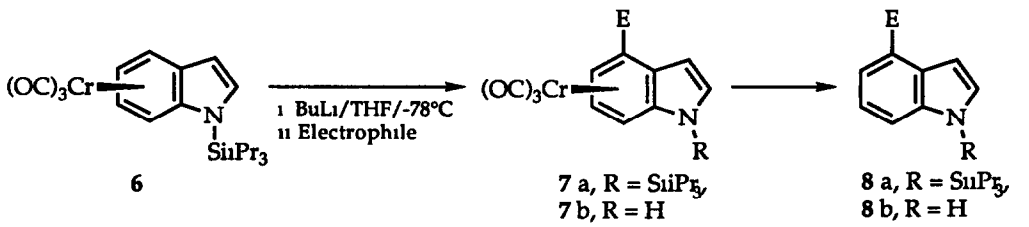
[a] Yield after decomplexation [b] The desilylated product was isolated

The results give some insight into four aspects of the transformation: the effects of variation of thiolate structure (Runs 1-7) shows slight reduction in yield for secondary thiols (Runs 2, 4) compared with primary thiols (Runs 1, 3, 5-7), the effects of halide leaving group (Runs 7, 8) shows unexpectedly[7] that the iodo- group is readily, though less efficiently, displaced The variation of electron density on the ring (Runs 9-13) indicates that the activating effect of the chromium unit is not negated by electron releasing groups and the presence of an

electron withdrawing (Run 13) does not improve the efficiency. The effect of steric congestion in the substrate by 2,6-disubstitution (Runs 14-16) is also minimal.

The principal limitation of this approach is the preference for fluorinated arene complexes as substrates[7], although as shown above, higher halides may be satisfactory. Because of its' electron withdrawing nature, the presence fluorine makes complexation more difficult and we have , for example, been unable to prepare difluorobenzenetricarbonylchromium(0) complexes Direct complexation of iodo- and bromo-arenes frequently results in dehalogenation and such compounds have to be made by indirect methods[8, 10a]

Scheme 2



6 7 a, R = SiiPr3, 7 b, R = H 8 a, R = SiiPr3, 8 b, R = H

Table 2 Electrophilic Thiation of Lithiated Arenechromium Complexes

Run	Complex	Reactant	Thiation Conditions	Product	Yield(%)
1	4	$(MeS)_2$	-78°C/2h	2, R = Me, R_n = H	45
2	4	S_8/MeI	-78°C/0 3h	2, R = Me, R_n = H	81
3	4	$(EtS)_2$	25°C/14h	2, R = Et, R_n = H	80
4	4	$(MeOCH_2CH_2S)_2$	25°C/14h	2, R = CH_2CH_2OMe, R_n = H	70
5	4	$(PhCH_2S)_2$	25°C/14h	2, R = CH_2Ph, R_n = H	26
6	4	$(4\text{-}MeC_6H_4S)_2$	-78°C/2h	2, R = 4-C_6H_4Me, R_n = H	39
7	4	$(PhS)_2$	-78°C/2 5h	2, R = Ph, R_n = H	54
8	4	PhSCl	25°C/17h	2, R = Ph, R_n = H	70
9	4	*N*-PhS-$(CO)_2C_6H_4$[a]	25°C/14h	2, R = Ph, R_n = H	35
10	4	*N*-PhS-$(CO)_2C_2H_4$[b]	-78°C/1h	2, R = Ph, R_n = H	58
11	4	$(PhSe)_2$	-78°C/14h	2, 'SR' = SePh, R_n = H	80
12	4	S_8	25°C/14h	2, R = H, R_n = H	31
13	6	$(EtS)_2$	-78°C/2h	8a, E = SEt	45
14	6	$(PhCH_2S)_2$	-78°C/2h	8b, E = SCH_2Ph	57
15	6	$(MeOCH_2CH_2S)_2$	-78°C/2h	7a, E = SCH_2CH_2OMe	23
				7b, E = SCH_2CH_2OMe	24

[a] *N*-Phenylthiophthalimide

[b] *N*-Phenylthiosuccinimide

The second approach (Schemes 1b, 2) avoids these additional steps by drawing upon the activating effect of a tricarbonylchromium(0) unit on the acidity of the ring protons[9]. Regioselective lithiation of arenechromium complexes has been widely studied and many novel specific functionalisations by this route have been discovered[5b, 10]. It was attractive therefore to apply this specificity to thiation reactions. Many electrophilic sulphur transfer agents have been reported[11], but we chose initially to use the simple symmetrical disulphides The results are presented in Table 2

Reaction of the benzene complexes (Runs 1-12) occurred in moderate to good yield without complications even though a variety of reaction conditions were used In contrast, the indole thiations (Runs 13-15) proved to be very sensitive to the nature of the product Mild conditions were used and a careful and constant work up Nevertheless, either or both of decomplexation (Runs 13, 14) and desilylation (Runs 14, 15) occurred readily.

The use of symmetrical disulphides is clearly inefficient for complicated sulphides but the sulphur transfer agents[11] (Runs 8-10) reacted satisfactorily and would obviate such a problem.

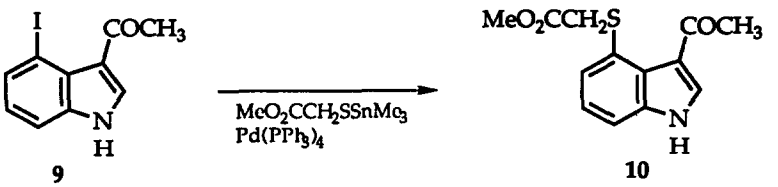
The lithiation/disulphide method is limited by the stability of the substrate or reactant to the highly basic reaction conditions Although transmetallation of lithium by copper(I) reagents may be expected to resolve this problem for sensitive reactants[12], the elevated temperatures required would be incompatible with the the metallated complexes and we chose, for sensitive substrates, to move to the very mild and neutral conditions offered by the palladium catalysed cross coupling reaction[13] (Schemes 1c, 3) For this process, the activation by a tricarbonylchromium unit is not required, though its presence does enable otherwise unreactive halides such as chloride to be used[14]

Table 3. Palladium Catalysed Coupling of Aryl Iodides and Alkylthiostannanes

Run	Aryl Iodide	Thiostannane	Product	Yield(%)
1	**5**, R_n = H	CH_2=$CHCH_2SSnMe_3$	**1**, R_n = H, R = CH_2CH=CH_2	100
2	**5**, R_n = H	$MeO_2CCH_2SSnMe_3$	**1**, R_n = H, R = CH_2CO_2Me	95
3	**5**, R_n = 4-OMe	$PhCH_2SSnMe_3$	**1**, R_n = 4-OMe, R = CH_2Ph	60
4	**8a**, E = I	$PhCH_2SSnBu_3$	**8a**, E = SCH_2Ph	56
5	**8a**, E = I	$MeO_2CCH_2SSnBu_3$	**8a**, E = SCH_2CO_2Me	62
6	**8a**, E = I	$MeO_2CCH_2SSnMe_3$	**8a**, E = SCH_2CO_2Me	98
7	**8a**, E = I	$EtO_2CCH_2SSnBu_3$	**8a**, E = SCH_2CO_2Et	70
8	**9**	$MeO_2CCH_2SSnMe_3$	**10**	83

Palladium catalysed coupling of thiolate ion itself is known[2i,15], but in order to achieve the mildest possible conditions, we chose to use thiostannanes in a sulphur analogue of a Stille reaction, a process for which there is one report in the literature[16] The results are given in Table 3

Scheme 3



9 **10**

In general these palladium catalysed reactions are higher yielding than the nucleophilic or electrophilic thiations and as we have observed in other couplings, the trimethylstannanes are better than the tributyl series Although the range of thiostannanes studied was not as wide as for the earlier thiations, the chemospecificity normally observed for palladium catalysed couplings suggests that the process will be very general Given a ready access to iodo- (or bromo-) arene substrates, the palladium cross coupling process appears to be the reaction of choice for aromatic thiation

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EXPERIMENTAL

General materials and techniques were as previously described[10g, 17]. Compounds or methods not previously reported in full are given below

Typical Procedure for the Nucleophilic Displacement of Halide in Haloarenetricarbonylchromium(0) Complexes by Thiolates — Sodium Hydride (2 equiv), and arenetricarbonylchromium(0)[16] (3) (1 equiv) were dissolved in THF (3–5ml), and the alkanethiol (2 equiv) was added *via* a syringe at room temperature The reaction was stirred at the stated temperature until reaction was complete (tlc assay) or for the indicated period of time Excess 2M hydrochloric acid was added and the resultant mixture extracted with ether (3 x 25ml) The combined organic phases were washed with aqueous sodium hydroxide (2 x 25ml) and water (2 x 25ml), dried ($MgSO_4$) and evaporated The residual oil was purified by flash chromatography over silica gel (typical eluant 98 2 petroleum ether ether) Compounds so prepared and not previously described in full were —

η^6-Butylthiobenzenetricarbonylchromium(0) (2, R_n = H, R = Bu) — Complex· (3, R_n = H) (169mg, 0 73mmol), butanethiol (0 2ml, 1 9mmol), reaction conditions. 25°C for 3h The *complex* (2, R_n = H, R = Bu) was isolated as a yellow oil (163mg, 74%), ν_{max} ($CHCl_3$) 1980, 1910 cm^{-1}, *m/z* 302 (M^+, 18%), 246 (15%), 218 (48%), 190 (4%), 176 (5%), 163 (3%), 162 (69%), 52 (100%), Found: M^+ 302 00640 $C_{13}H_{14}CrO_3S$ requires· 302 00688

η^6-Cyclohexylthiobenzenetricarbonylchromium(0) (2, R_n = H, R = C_6H_{11}) — Complex (3, R_n = H) (137mg, 0 59mmol), cyclohexanethiol (0 15ml, 1 2mmol); reaction conditions. 25°C for 14h

The *complex* (2, R_n = H, R = C_6H_{11}) was isolated as a yellow oil (106mg, 55%), ν_{max} ($CHCl_3$) 1970, 1900 cm^{-1}; *m/z* 328 (M^+, 17%), 272 (15%), 244 (53%), 192 (1 5%), 52 (100%) Found: M^+ 328.02240. $C_{15}H_{16}CrO_3S$ requires: 328 02253.

η^6-*2-Propenylthiobenzenetricarbonylchromium(0)* (2, R_n = H, R = $CH_2CH{=}CH_2$) — Complex· (3, R_n = H) (301mg, 1 3mmol); 2-propenethiol (0 2ml, 2 5mmol), reaction conditions· 25°C for 14h The *complex* (2, R_n = H, R = $CH_2CH{=}CH_2$) was isolated as a yellow solid (268mg, 72%), ν_{max} ($CHCl_3$) 1975, 1900 cm^{-1}; δ_H ($CDCl_3$, 60MHz) 3.5 (2H,d,*J* 7Hz), 5 0-5 6 (8H, m); *m/z* 286 (M^+, 11%), 258 (0 2%), 230 (3 5%), 202 (43%), 150 (2%), 109 (1%), 52 (100%)

η^6-*Phenylthiobenzenetricarbonylchromium(0)* (2, R_n = H, R = Ph) — Complex. (3, R_n = H) (161mg, 0 69mmol), thiophenol (0.2ml, 1 95mmol); reaction conditions. 67°C for 6h The *complex* (2, R_n = H, R = Ph) was isolated as yellow crystals (117mg, 53%), m.p. 70 5-71 5°C; ν_{max} ($CHCl_3$) 1975, 1910 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 5 1-5 5 (5H, m), 7 3-7 65 (5H, m); *m/z* 322 (M^+, 20%), 266 (12%), 238 (100%), 186 (22%). Found: C, 55 65, H, 3 01 $C_{15}H_{10}CrO_3S$ requires C, 55 90, H, 3 13%

η^6-*Methoxycarbonylmethylthiobenzenetricarbonylchromium(0)* (2, R_n = H, R = CH_2CO_2Me) — Complex: (3, R_n = H) (210mg, 0 9mmol), methyl thioglycolate (0 2ml, 2 2mmol); reaction conditions 67°C for 21h The *complex* (2, R_n = H, R = CH_2CO_2Me) was isolated as an orange oil (172mg, 60%), ν_{max} ($CHCl_3$) 1980, 1910, 1735 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 3 35 (2H, s), 3 70 (3H, s), 5 15-5 60 (5H, m), *m/z* 318 (M^+), 290 (0 7%), 262 (3 5%), 234 (9%), 182 (64%), 123 (100%) Found M^+ 317 9661 $C_{12}H_{10}CrO_5S$ requires 317 9654

η^6-*(2,2-Diethoxyethylthio)benzenetricarbonylchromium(0)* [2, R_n = H, R = $CH_2CH_2(OMe)_2$] — Complex (3, R_n = H) (214mg, 0 92mmol), 2,2-diethoxyethanethiol (222mg, 1 48mmol), reaction conditions 25°C for 2h The *complex* [2, R_n = H, R = $CH_2CH_2(OMe)_2$] was isolated as a red oil (330mg, 99%), ν_{max} ($CHCl_3$) 1980, 1905 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 1 2 (6H, t, *J* 7Hz), 3 0 (2H, d, *J*5 9Hz), 3 55 (4H, m), 4 6 (1H, t, *J* 5 5Hz), 5 0-5 5 (5H, m), *m/z* 362 (M^+, 15%), 306 (8%), 278 (35%), 226 (9%), 181 (9%), 135 (21%), 109 (10%), 103 (100%) Found M^+ 362.0295 $C_{15}H_{18}CrO_5S$ requires 362 0280 Found C, 49.95, H, 5 08. $C_{15}H_{18}CrO_5S$ requires C, 49 72, H, 5 01%

η^6-*Benzylthiobenzenetricarbonylchromium(0)* (2, R_n = H, R = CH_2Ph) — 1 Complex (3, R_n = H) (159mg, 0 68mmol), α-toluenethiol (253mg, 2 04mmol), reaction conditions. mixing at 0°C → room temperature to completion (tlc) The *complex* (2, R_n = H, R = CH_2Ph) was isolated as yellow crystals (205mg, 90%) m p 108-109°C, ν_{max} ($CHCl_3$) 1975, 1900 cm^{-1}, δ_H ($CDCl_3$, 90MHz) 4 0 (2H, s) 5 25 (5H, m), 7 3 (5H, m); *m/z* 336 (M^+, 6%), 252 (34%), 200 (7%), 91 (28%), 52 (100%) Found C, 57 08, H, 3 40, S, 9 27 $C_{16}H_{12}CrO_3S$ requires C, 57 14, H, 3 60, S, 9 53%

11 Complex η^6-iodobenzenetricarbonylchromium(0) (81mg, 0 24mmol), α-toluenethiol (0.1ml, 0 85mmol); reaction conditions 25°C for 14h. The product (2, R_n = H, R = CH_2Ph) was isolated as yellow crystals (32mg, 52%) m p 106-107°C; spectroscopically identical to the material obtained above

η^6-*1-Benzylthio-2-methylbenzenetricarbonylchromium(0)* (2, R_n = 2-Me, R = CH_2Ph) — Complex (3, R_n = 2-Me) (43mg, 0 17mmol), α-toluenethiol (63mg, 0 51mmol), reaction

conditions: mixing at 0°C → room temperature to completion (tlc). The *complex* (2, R_n = 2-Me, R = CH_2Ph) was isolated as a yellow oil (44mg, 72%), ν_{max} ($CHCl_3$) 1972, 1895 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 2.19 (3H, s), 4.02 (2H, s), 5.0-5.4 (4H, m), 7.28 (5H, s); *m/z* 350 (M^+), 226, 174, 91 (100%) Found: M^+ 350.0077. $C_{17}H_{14}CrO_3S$ requires: 350 0069.

η^6-1-Benzylthio-2-methoxybenzenetricarbonylchromium(0) (2, R_n = 2-OMe, R = CH_2Ph) — Complex: (3, R_n = 2-OMe) (178mg, 0 68mmol); α-toluenethiol (253mg, 2.04mmol); reaction conditions: mixing at 0°C → room temperature to completion (tlc) The *complex* (2, R_n = 2-OMe, R = CH_2Ph) was isolated as yellow needles (224mg, 90%), m p. 97-100°C, ν_{max} ($CHCl_3$) 1975, 1902 cm^{-1}, δ_H ($CDCl_3$, 90MHz) 3 76 (3H, s), 3.95, 4 20 (2H, ABq, *J* 12Hz), 4 77 (1H, t, *J* 6Hz), 5 05 (1H, d, *J* 6Hz), 5 35 (1H, dt, *J* 6, 1 5Hz), 5.63 (1H, dd, *J* 6, 1 5Hz), 7 26 (5H, s); *m/z* 366 (M^+), 282, 267, 230, 91 (100%) Found. C, 55 74, H, 3 74; S, 9 00 $C_{17}H_{14}CrO_4S$ requires. C, 55 73; H, 3 85; S, 8 75%

η^6-1-Benzylthio-4-methoxybenzenetricarbonylchromium(0) (2, R_n = 4-OMe, R = CH_2Ph) — i. Complex: (3, R_n = 4-OMe)[16] (242mg, 0 92mmol), α-toluenethiol (342mg, 2 76mmol), reaction conditions: mixing at 0°C → room temperature to completion (tlc) The *complex* (2, R_n = 4-OMe, R = CH_2Ph) was isolated as yellow needles (281mg, 83%), m p 58-60°C; ν_{max} ($CHCl_3$) 1973, 1897, 1455 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 3 55 (3H, s), 3 87 (2H, s), 4 91 (2H, d, *J* 7Hz), 5 45 (2H, d, *J* 7Hz), 7.16 (5H, s), *m/z* 366 (M^+), 282, 230, 91 (100%) Found: C, 55 65; H, 3.71, S, 8.88 $C_{17}H_{14}CrO_4S$ requires. C, 55 73, H, 3 85; S, 8 75%

ii Complex. (3, R_n = 4-OMe-2-$SiMe_3$)[19] (240mg, 0 79mmol), α-toluenethiol. (294mg, 2 37mmol), reaction conditions mixing at 0°C → room temperature to completion (tlc) The *product* (2, R_n = 4-OMe, R = CH_2Ph) was isolated as yellow needles (237mg, 79%), identical with the material obtained above

2-Methoxycarbonyl-1-benzylthiobenzene (1, R_n = 2-CO_2Me, R = CH_2Ph) —. Complex: (3, R_n = 2-CO_2Me)[19] (142mg, 0 49mmol); α-toluenethiol (182mg, 1 47mmol); reaction conditions: mixing at 0°C → room temperature, 2h Work up the precipitated product was dissolved in ethyl acetate and irradiated (500watt tungsten lamp, with cooling) overnight, then as before gave the *product* (1, R_n = 2-CO_2Me, R = CH_2Ph) as colourless crystals (87mg, 67%), m.p. 65 5°c (lit.[20] m p 65 5-67°C), ν_{max} ($CHCl_3$) 1709, 1590 cm^{-1}, δ_H ($CDCl_3$, 90MHz) 3 92 (3H, s), 4 17 (2H, s), 7 2-7.5 (8H, m), 8 0 (1H, dd, *J* 7, 1Hz), *m/z* 258 (M^+), 226, 167, 91 (100%)

η^6-1-Benzylthio-2-methoxy-6-methylbenzenetricarbonylchromium(0) (2, R_n = 2-OMe-6-Me, R = CH_2Ph) — Complex: (3, R_n = 2-OMe-6-Me)[19] (156mg, 0 57mmol), α-toluenethiol (212mg, 1 71mmol), reaction conditions: mixing at 0°C → room temperature to completion (tlc). The *complex* (2, R_n = 2-OMe-6-Me, R = CH_2Ph) was isolated as a yellow solid (166mg, 78%), ν_{max} ($CHCl_3$) 1970, 1900, 11602, 1475 cm^{-1}, δ_H ($CDCl_3$, 250MHz) 2 13 (3H, s), 3 75-3 90 (4H, m), 4 08 (1H, d, *J* 12Hz), 4 73 (1H, d, *J* 6.5Hz), 4 98 (1H, d, *J* 6.5Hz), 5 55 (1H, t, *J* 6 5Hz), 7 12-7 35 (5H, s), *m/z* 380 (M^+), 296, 244, 91 (100%) Found. C, 56 83, H, 4 10 $C_{18}H_{16}CrO_4S$ requires: C, 56 84, H, 4 24%

η^6-1-Benzylthio-4-methoxy-2-methylbenzenetricarbonylchromium(0) (2, R_n = 4-OMe-2-Me, R =

CH_2Ph). — Complex: (3, R_n = 4-OMe-2-Me)†[19] (469mg, 1.70mmol); α-toluenethiol (632mg, 5 1mmol); reaction conditions: mixing at 0°C → room temperature to completion (tlc). The *complex* (2, R_n = 4-OMe-2-Me, R = CH_2Ph) was isolated as a yellow oil (506mg, 78%); ν_{max} ($CHCl_3$) 1970, 1895, 1602, 1525, 1460 cm^{-1}; *m/z* 380 (M^+), 282, 91 (100%). Found: C, 56.60; H, 4 25. $C_{18}H_{16}CrO_4S$ requires· C, 56.84; H, 4.23%

η⁶-1-Benzylthio-5-methoxy-2-methylbenzenetricarbonylchromium(0) (2, R_n = 5-OMe-2-Me, R = CH_2Ph) — Complex: (3, R_n = 5-OMe-2-Me-6-$SiMe_3$)[19] (138mg, 0.40mmol); α-toluenethiol (150mg, 1 2mmol); reaction conditions: mixing at 0°C → room temperature to completion (tlc) Work up by initial treatment with TBAF (0.5mmol, 1M in THF), then as before gave the *complex* (2, R_n = 5-OMe-2-Me, R = CH_2Ph) as a yellow oil (119mg, 78%); ν_{max} ($CHCl_3$) 1965, 1890, 1460 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 2.07 (3H, s), 3.56 (3H, s), 4 06 (2H, s), 5.03 (1H, dd, *J* 7, 1.5Hz), 5 20 (1H, d, *J* 1.5Hz), 5.46 (1H, d, *J* 7Hz), 7 32 (5H, s), *m/z* 380 (M^+), 296, 244, 204, 153, 91 (100%) Found M^+, 380 0157. $C_{18}H_{16}CrO_4S$ requires· 380.0174

Typical Procedure for the Lithiation/Electrophilic Quench of η⁶-Arenetricarbonylchromium(0) Complexes. — Butyl lithium (1 6M, 1 1 equiv) was added to the η⁶-arenetricarbonylchromium(0) complex (1.0 mmol) in THF (50ml) at –78°C After 1 h. at this temperature, the electrophile[11, 21] (1 1 mmol) in THF (5ml) was added and the mixture stirred at the stated temperature for the indicated period of time Ammonium chloride (20ml, 2.8M, 56mmol) and ether (25ml) were added, the mixture shaken thoroughly and the layers separated The aqueous phase was extracted with ether (3 x 25ml), the combined ethereal extracts dried ($MgSO_4$), the solvent evaporated under reduced pressure and the residue purified by flash chromatography Compounds so prepared and not previously reported in full are:—

η⁶-Thioanisoletricarbonylchromium(0) (2, R_n = H, R = Me) – ı Complex: (4, R_n = H) (213 3mg, 1 0mmol), electrophile. dimethyl disulphide (0 11ml, 1.2mmol); quench conditions: 14h at 25°C The product (2, R_n = H, R = Me) was isolated as yellow crystals (210 5mg, 81%), m.p 104–105°C; ν_{max} ($CHCl_3$) 1980, 1900, 1430 cm^{-1}, δ_H ($CDCl_3$, 60MHz) 2 5 (3H, s), 5 3 (5H, m), *m/z* 260 (M^+), 204 176, 161, 124, 109 Found. C, 46 31, H, 3 06 Calc for $C_{10}H_8CrO_3S$· C, 46 16, H, 3 10%.

ıı Complex· (4, R_n = H) (433mg, 2 0mmol), electrophile sulphur (93mg, 2 9mmol); quench conditions 0 3h at -78°C Work up with methyl iodide (0 5ml, 8.0mmol, 1h) gave (2, R_n = H, R = Me) as yellow crystals (254mg, 48%), m.p 102-103°C, spectroscopically identical with the above material.

η⁶-Thiophenetoletricarbonylchromium(0) (2, R_n = H, R = Et) – Complex: (4, R_n = H) (436mg, 2 04mmol), electrophile: diethyl disulphide (1 0ml, 11 0mmol); quench conditions 14h at 25°C The *complex* (2, R_n = H, R = Et) was isolated as yellow crystals (447 8mg, 80%), m p 34°C; ν_{max} ($CHCl_3$) 1980, 1900 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 1 3 (3H, t), 2 9 (2H, q), 5 4 (5H, m); *m/z* 274 (M^+, 36%), 218 (30%), 190 (58%), 138 (22%), 123 (14%), 52 (100%) Found. C, 47 91; H, 3.60. $C_{11}H_{10}CrO_3S$

† This substance contained 2 5% each of 4-fluoroanisole complex and 3,5-dimethyl-4-fluoroanisole complex

requires: C, 48.17; H, 3.68%.

η^6-*(2-Methoxyethylthio)benzenetricarbonylchromium(0)* (**2**, R_n = H, R = CH_2CH_2OMe) — Complex· (**4**, R_n = H) (381mg, 1.78mmol); electrophile. 2-methoxyethyl disulphide (370mg, 2 03mmol); quench conditions: 14h at 25°C. The *complex* (**2**, R_n = H, R = CH_2CH_2OMe) was isolated as yellow crystals (380mg, 70%), m.p. 66-7°C; ν_{max} ($CHCl_3$) 1975, 1905 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 3 1 (2H, t, *J* 7Hz), 3.4 (3H, s), 3 7 (2H, t, *J* 7Hz), 5.2-5.6 (5H, m), *m/z* 304 (M^+, 19%), 248 (12%), 220 (37%), 168 (38%), 123 (42%), 110 (27%), 52 (100%). Found: C, 47.32; H, 3.88; S, 10 27 $C_{12}H_{12}CrO_4S$ requires: C, 47.37; H, 3 98; S, 10.54%.

η^6-*Benzylthiobenzenetricarbonylchromium(0)* (**2**, R_n = H, R = CH_2Ph). — Complex: (**4**, R_n = H) (489mg, 2 28mmol); electrophile. dibenzyl disulphide (617mg, 2 5mmol); quench conditions 14h at 25°C The product (**2**, R_n = H, R = CH_2Ph) was isolated as yellow crystals (198mg, 26%), m p 108-9°C identical with the material obtained above.

η^6-*p-Tolylthiobenzenetricarbonylchromium(0)* (**2**, R_n = H, R = 4-MeC_6H_4). — Complex: (**4**, R_n = H) (233mg, 1 09mmol), electrophile. di-*p*-tolyl disulphide (329mg, 1 33mmol); quench conditions· 2h at –78°C The *complex* (**2**, R_n = H, R = 4-MeC_6H_4) was isolated as yellow crystals (143mg, 39%), m p 110-111 5°C, ν_{max} ($CHCl_3$) 1975, 1900 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 2 4 (3H,s), 5 1-5 5 (5H, m), 7 25 (2H, d), 7 50 (2H, d); *m/z* 336 (M^+, 17%), 280 (8%), 252 (100%), 200 (37%) Found. C, 57.14, H, 3.55 $C_{16}H_{12}CrO_3S$ requires· C, 57 14, H, 3 60%.

η^6-*Phenylthiobenzenetricarbonylchromium(0)* (**2**, R_n = H, R = Ph). — i Complex. (**4**, R_n = H) (459mg, 2 14mmol); electrophile. diphenyl disulphide (610mg, 2.79mmol); quench conditions 2 5h at –78°C The *product* (**2**, R_n = H, R = Ph) was isolated as yellow crystals (370mg, 54%), m p. 70-1°C; spectroscopically identical with the material obtained above

ii Complex (**4**, R_n = H) (214mg, 1 0mmol), electrophile benzenesulphenyl chloride (144mg, 1 0mmol); quench conditions 17h at 25°C, product (**2**, R_n = H, R = Ph). yellow crystals (225mg, 70%) m p. 70-71 5°C, spectroscopically identical with the material obtained above

iii Complex (**4**, R_n = H) (429mg, 2.0mmol), electrophile. *N*-phenylthiophthalimide (646mg, 2 5mmol); quench conditions 14h at 25°C, product (**2**, R_n = H, R = Ph) yellow crystals (223mg, 35%) m p 70-71°C, spectroscopically identical with the material obtained above

iv Complex (**4**, R_n = H) (260mg, 1.20mmol), electrophile· *N*-phenylthiosuccinimide (274mg, 1 32mmol); quench conditions· 1h at –78°C, product (**2**, R_n = H, R = Ph) yellow crystals (224mg, 58%) m.p 66-67 5°C, spectroscopically identical with the material obtained above

η^6-*Phenylselenobenzenetricarbonylchromium(0)* (**2**, R_n = H, RS = SePh) — Complex· (**4**, R_n = H) (170mg, 0 79mmol), electrophile diphenyl diselenide (352mg, 1 13mmol); quench conditions 14h at –78°C The *complex* (**2**, R_n = H, RS = SePh) was isolated as yellow crystals (232mg, 80%), m p 76 5-77 5°C, ν_{max} ($CHCl_3$) 1980, 1905 cm^{-1}, δ_H ($CDCl_3$, 250MHz) 5 20 (1H, t, *J* 7Hz), 5 30 (2H, t, *J* 7Hz), 5 38 (2H, d, *J* 7Hz), 7 4 (3H, m), 7 6 (2H, m), *m/z* 370 (M^+, 12%), 314 (4%), 286 (55%), 234 (4%), 77 (7%), 52 (100%). Found. C, 48 70, H, 2 59 $C_{15}H_{10}CrO_3Se$ requires: C, 48 80, H, 2 73%

η^6-*Thiophenoltricarbonylchromium(0)* (**2**, R_n = H, R = H) — Complex: (**4**, R_n = H) (441mg, 2 1mmol), electrophile sulphur (102mg, 3 2mmol), quench conditions 14h at 25°C The

complex (**2**, R_n = H, R = H was isolated as yellow crystals (158mg, 31%), m.p. 162°C; ν_{max} ($CHCl_3$) 1980, 1920 cm^{-1}, δ_H ($CDCl_3$, 90MHz) 5.35 (3H, m), 5.6 (2H, m); *m/z* 218 (M^+), 110 (81%), 109 (40%), 77 (19%). Found. C, 44.10; H, 2.46. $C_9H_6CrO_3S$ requires: C, 43.91; H, 2.46%.

4-Ethylthio-1-triisopropylsilylindole (**1**, R_n = 2,3-CH=CH-N($SiiPr_3$)-, R = Et). — Complex: η^6-(1-triisopropylindole)tricarbonylchromium(0)[22] (529mg, 1 29mmol), electrophile: diethyl disulphide (348mg, 2.84mmol); quench conditions: 2h at –78°C. The *product* (**1**, R_n = 2,3-CH=CHN($SiiPr_3$)-, R = Et) was isolated as a yellow oil (195mg, 45%); ν_{max} (film) 2960, 2870, 1590, 1560, 1510 cm^{-1}; δ_H ($CDCl_3$, 250MHz) 1 14 (18H, dd), 1 28 (3H, t), 1 78 (3H, septet), 3.01 (2H, q), 6.70 (1h, dd), 7.07-7 13 (2H, m), 7.39 (1H, d), 7 45 (1H, ddd); *m/z* 333 (M^+, 100%), 304 (2%), 175 (30%), 147 (6%)

4-Benzylthioindole (**1**, R_n = 2,3-CH=CH-N($SiiPr_3$)-, R = CH_2Ph) — Complex· η^6-(1-triisopropylindole)tricarbonylchromium(0)[22] (416mg, 1 02mmol), electrophile: dibenzyl disulphide (521mg, 2 1mmol), quench conditions. 2h at –78°C The *product* (**1**, R_n = 2,3-CH=CH-N($SiiPr_3$)-, R = CH_2Ph) was isolated as a yellow gum (140mg, 57%); ν_{max} ($CHCl_3$) 3480, 2930, 2870, 1605, 1575 cm^{-1}; δ_H ($CDCl_3$, 90MHz) 4.2 (2H, s), 6 7 (1h, dd), 6 95-7 35 (9H, m), 8.0 (1H, br s); *m/z* 239 (M^+), 148

η^6-*4-(2-Methoxyethylthio)-1-triisopropylsilylindoletricarbonylchromium(0)* (**2**, R_n = 2,3-CH=CH-N($SiiPr_3$)-, R = CH_2CH_2OMe) and η^6-*4-(2-Methoxyethylthio)indoletricarbonylchromium(0)* (**2**, R_n = 2,3-CH=CH-NH-, R = CH_2CH_2OMe) — Complex· η^6-(1-triisopropylindole)tricarbonylchromium(0)[22] (410mg, 1 0mmol), electrophile· bis-2-methoxyethyl disulphide (450mg, 2 47mmol), quench conditions 2h at –78°C Flash chromatography gave·—

i the *complex* (**2**, R_n = 2,3-CH=CH-N($SiiPr_3$)-, R = CH_2CH_2OMe) (117mg, 23%); ν_{max} ($CHCl_3$) 1955, 1875 cm^{-1}, δ_H ($CDCl_3$, 250MHz) 1.14 (9H, d, *J* 7 5Hz), 1 22 (9H, d, *J* 7 5Hz), 1 82 (3H, septet, *J* 7 5Hz), 3 22 (2H, t, *J* 6 3Hz), 3 27 (3H, s), 3 65 (1H, t, *J* 6 3Hz), 3 66 (1H, t, *J* 6 3Hz), 5 57 (2H, m), 6 54 (1H, dd, *J* 6 5, 1 4Hz), 6 71 (1H, d, *J* 3 3Hz), 7 62 (1H, d, *J* 3 5Hz); *m/z* 499 (M^+, 0 3%), 415 (3%), 363 (100%), 320 (2 5%), 305 (14%), 262 (16%) Found C, 55 22, H, 6 68; N, 2 82 $C_{23}H_{33}CrNO_4SSi$ requires, C, 55 29, H, 6 66, N, 2 80%

ii the *complex* (**2**, R_n = 2,3-CH=CH-NH-, R = CH_2CH_2OMe) (82mg, 24%), ν_{max} ($CHCl_3$) 3470, 1960, 1875 cm^{-1}, δ_H ($CDCl_3$, 250MHz) 3 23 (2H, t), 3 30 (3H, s), 3 67 (2H, t), 5 49 (1H, m), 5 59 (1H, m), 6 39 (1H, d), 6 56 (1H, d), 7 56 (1H, d), *m/z* 343 (M^+, 0 3%), 287, 259 (42%), 207 (1%), 162 (0 6%), 148 (2%) Found C, 48 87, H, 3 69; N, 4 06 $C_{14}H_{13}CrNO_4S$ requires C, 48 98, H, 3 82, N, 4 08%

2–Propenethiotributylstannane[23] —Tributyltin chloride (9 84 g, 30 0 mmol) was added dropwise over 15 minutes to a stirred DMF (20 ml) solution of sodium allylthiolate (2.96 g, 30 0 mmol) at room temperature and the mixture left to react overnight A 1 1 petroleum ether–water mixture (20 ml) was added and the petroleum ether layer washed with water (15 ml) The aqueous phase was washed with petroleum ether (2 x 15 ml) and the combined organic solution dried ($MgSO_4$) and the solvents removed The residual oil was distilled (kugelrohr oven temp 210–212°C / 8 Torr) to give *2–propenethiotributylstannane* as a straw

coloured oil (8.16g, 75%); ν_{max} (film) 2957, 2922, 2872, 2853, 1464 cm^{-1}; δ_H ($CDCl_3$) 0.90 (9H, t, *J* 7 4Hz), 1.11 (6H, m), 1.33 (6H, m), 1.55 (6H, m), 3.22 (2H, br sextet, J_{C-H} 6.7Hz, J_{Sn-H} 28Hz), 4 95 (1H, br d, *J* 9 9Hz), 5.10 (1H, ddd, *J* 16.5, 1 4, 1.1Hz), 5 88 (1H, ddt, *J* 16 5, 9.9, 6.9Hz), *m/z* 307 (96%), 303 (41%) 251 (75%), 249 (56%), 193 (43%), 153 (48%) Found: C, 49.45; H, 9.11; S, 8.90. $C_{15}H_{32}SSn$ requires C, 49.61; H, 8.88, S, 8 83%.

2-Propenethiotrimethylstannane — Trimethyltin chloride (12.01g, 60.0mmol) in tetrachloromethane (15 ml) was added, *via* a syringe, to a rapidly stirred solution of technical grade allylthiol (4.45 g, 85% pure 52 0 mmol) and triethylamine (6 68 g, 66mmol) in carbon tetrachloride (300 ml). After 24 h, the mixture was filtered and washed with 5% aqueous acetic acid (50 ml) and water (2 x 50 ml) before drying ($MgSO_4$) and careful removal of the solvents Kugelrohr distillation (oven temp. 50°C / 0 3 Torr) gave *2-propenethiotrimethylstannane* as a colourless oil (8.12g, 65%) ν_{max} (film) 3080, 2978, 2915, 1634, 1434 cm^{-1}; δ_H ($CDCl_3$) 0 40 (9H, s+d, $J_{^{119}Sn-Me}$ 56Hz), 3.19 (2H, ddd, J_{H-H} 7 0 1 5, 1 5Hz, d+d, $J_{^{119}Sn-H}$ 41.5Hz, $J_{^{117}Sn-H}$ 27 5Hz), 4.93 (1H, ddd, *J* 9 5, 1.5, 1 5Hz), 5 06 (1H, ddt, *J* 17 0, 1 5, 1 5Hz), 5.84 (1H, ddt, *J* 17.0, 9 5, 7 0Hz); *m/z* 238 (M^+, 2%), 209 (26%), 179 (10%), 165 (18%), 32 (100%), Found: C, 30 64; H, 6 09. $C_{15}H_{32}SSn$ requires C, 30 42; H, 6.09%

Methoxycarbonylmethylthiotrimethylstannane — Trimethyltin chloride (5 95g, 29 9mmol) in tetrachloromethane (9 ml) was added, *via* syringe, at room temperature to a rapidly stirred tetrachloromethane (150ml) solution of triethylamine (3.63g, 35 9mmol) and methyl thioglycolate (3 44g, 32 4mmol) under nitrogen The resulting white slurry was vigorously stirred for 2h before being filtered (Celite) and washed with 5% aqueous acetic acid (50 ml) and water (2 x 50 ml) After drying ($MgSO_4$), the solvents were removed and the residue purified by kugelrohr distillation (oven temp 70°C / 0 06 Torr) to give the *methoxycarbonylmethylthiotrimethylstannane* as a colourless oil (6 40g, 23.8mmol, 80%); ν_{max} (film) 2991, 2952, 2916, 1733, 1437cm^{-1}; δ_H ($CDCl_3$) 0 44 (9H, s + dd, $J_{^{119}Sn-H}$ 33Hz, $J_{^{117}Sn-H}$ 31Hz), 3 23 (2H, s + dd, $J_{^{119}Sn-H}$ 36 Hz, d, $J_{^{117}Sn-H}$ 35Hz), 3 67 (3H, s), δ_C ($CDCl_3$) –4 9, 27 8, 52 5, 172 9, *m/z* 255 (100%), 254 (31%), 253 (74%), 251 (43%), 223 (40%), 221 (29%), 165 (19%); Found C, 26.92, H, 5.42; S, 11 78. $C_6H_{14}O_2SSn$ requires C, 26 80; H, 5 25, S, 11 92%.

Ethoxycarbonylmethylthiotributylstannane — Tri-n-butyltin chloride (8 2 ml, 9.76 g, 30 mmol) was added to a stirred solution of ethyl thioglycolate (3 3 ml, 3 61 g, 30 mmol) and triethylamine (4 9 ml, 3 54 g, 35 mmol) in carbon tetrachloride (200 ml). After 1 hour, the mixture was filtered and the solvents removed to reveal a golden yellow oil. This was distilled to give *ethoxycarbonylmethylthiotributylstannane* as a colourless oil (9.22 g, 22.5 mmol, 75%); b p 116°C / 0.3 Torr ; ν_{max} (film) 2958, 2924, 2872, 2854, 1734, 1464 cm^{-1}, δ_H ($CDCl_3$) 0.86 (12H, m), 1 10-1 25 (12H, m), 1 45-1 65 (6H, m), 3 16 (2H, s), 4 12 (2H, q, *J* 7 7Hz); *m/z* 359 (20%) ,353 (51%), 351 (38%), 269 (50%), 267 (37%), 265 (19%) 28 (100%) Found C, 47 12; H, 8 52, S, 7 51 $C_{16}H_{34}O_2SSn$ requires C, 46 96; H, 8 40; S, 7 83%

Typical Procedure for the Palladium Catalysed Cross Coupling Reactions. — A solution of alkylthiotrialkylstannane (1 1 equiv) in toluene was added to the arene (1 equiv) and

tetrakistriphenylphosphinepalladium(0) (5-10 mol%) in toluene (or other as stated) and the mixture heated to reflux under a nitrogen atmosphere until reaction was complete (t.l.c. assay, 4-30 h). 10% aqueous potassium fluoride and ether were added, the layers separated and the aqueous phase washed with ether (3 x 20ml). The combined organic phases were washed with 10% aqueous potassium fluoride (2 x 20ml) and water (20ml), dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography over silica gel (typical eluant: petroleum ether – ether 95 : 5). So prepared were:—

2-Propenylthiobenzene (**1**, R_n = H, R = $CH_2CH{=}CH_2$) — Arene· iodobenzene (200mg, 1 0mmol); tin reagent: 2-propenethiotrimethylstannane (260mg, 1 1mmol); catalyst – (110mg, 10 mol%); solvent: – (25ml) The product (**1**, R_n = H, R = $CH_2CH{=}CH_2$) was obtained as a colourless oil (150mg, 100%); ν_{max} (film) 3077, 3059, 2918, 1637, 1583, 1480cm^{-1}; δ_H ($CDCl_3$) 3 54 (2H, ddd, *J* 7.0, 1 0, 1 0Hz), 5 06 (1H, ddt, *J* 10.0, 1 0, 1 0Hz), 5 12 (1H, ddt, *J* 17.0, 1.0, 1.0Hz), 5.87 (1H, ddt, *J* 17.0, 10.0, 7.0Hz), 7.22 (5H, m); *m/z* 150 (M^+, 12%) 125 (58%), 117 (24%), 110 (100%), 109 (38%)

Methoxycarbonylmethylthiobenzene (**1**, R_n = H, R = CH_2CO_2Me).— Arene: iodobenzene (200mg, 1.0mmol); tin reagent. methoxycarbonylmethylthiotrimethylstannane (280mg, 1 05mmol), catalyst – (47mg, 4mol% + triphenylphosphine 42mg, 16mol%); solvent: – (25ml) The product (**1**, R_n = H, R = CH_2CO_2Me) was isolated as a colourless oil (170mg, 95%); ν_{max} (film) 2952, 1741, 1584, 1483 cm^{-1}; δ_H ($CDCl_3$) 3 65 (2H, s), 3.71 (3H, s), 7.27 (3H, m), 7.41 (2H, m); δ_C ($CDCl_3$) 36.5, 52.6, 127 0, 127 2, 129.1, 135.0, 170.2, *m/z* 182 (M^+, 79%), 124 (9%), 123 (100%), 109 (12%) Found: C, 59.42; H, 5.54; S, 17.60. $C_9H_{10}O_2S$ requires C, 59.32; H, 5.53; S, 17.59%.

4-Benzylthioanisole (**1**, R_n = 4-OMe, R = CH_2Ph) — Arene: 4-iodoanisole (237mg, 1 01mmol); tin reagent: benzylthiotributylstannane (423mg, 1 02mmol); catalyst – (77mg, 6.6mol%); solvent. – (20ml) The product (**1**, R_n = 4-OMe, R = CH_2Ph) was obtained as colourless crystals (140mg, 60%), m p 47.5-48.5°C (lit.[24] 46-47°C), ν_{max} ($CHCl_3$) 2940, 1590, 1570, 1485 cm^{-1}; δ_H ($CDCl_3$, 60MHz) 3 8 (3H, s), 4.0 (2H, s), 6.8 (2H, d), 7.25 (5H, s), 7.3 (2H, d); *m/z* 230 (M^+, 35%), 216 (3.4%), 200 (7%), 139 (10%), 91 (100%).

4-Benzylthio-1-triisopropylsilylindole (8a, E = SCH_2Ph) — Arene: 4-iodo-1-triisopropylsilylindole[10f] (603mg, 1.51mmol); tin reagent: benzylthiotributylstannane (713mg, 1 73mmol); catalyst – (86mg, 5mol%); solvent. – (10ml) The product (8a, E = SCH_2Ph) was obtained as colourless crystals (334mg, 56%), m p. 80-81°C, ν_{max} ($CHCl_3$) 2930, 2870, 1605, 1590, 1560, 1495 cm^{-1}; δ_H ($CDCl_3$, 250MHz) 1 14 (18H, d, *J* 7 6Hz), 1 77 (3H, septet, *J* 7.6Hz), 4.24 (2H, s), 6 71 (1H, dd, *J* 3 2, 0 8Hz), 7.06 (2H, m), 7 24 (5H, m), 7 40 (1H, d, *J* 3 2Hz), 7.46 (1H, ddd, *J* 5.5, 3 5, 0 75Hz); *m/z* 395 (M^+, 1 4%), 304 (0 5%), 230 (20%), 123 (20%), 91 (100%). Found: C, 72.97; H, 8 43, N, 3 50 $C_{24}H_{33}NSSi$ requires: C, 72 85; H, 8 41, N, 3 54%

4-Methoxycarbonylmethylthio-1-triisopropylsilylindole (8a, E = SCH_2CO_2Me). — 1. Arene 4-iodo-1-triisopropylsilylindole[10f] (492mg, 1.23mmol), tin reagent. methoxycarbonylmethylthiotributylstannane (626mg, 1.58mmol), catalyst – (88mg, 6 2mol%); solvent. – (10ml). The product (8a, E = SCH_2CO_2Me) was obtained as a colourless oil (287mg, 62%), ν_{max} (film) 2948, 2868, 1741, 1467 cm^{-1}, δ_H ($CDCl_3$, 250MHz) 1 14 (18H, d, *J* 7 6Hz), 1.70 (3H, septet, *J* 7.6Hz), 3.67

(3H, s), 3.73 (2H, s), 6.80 (1H, dd, *J* 3.2, 0.7Hz), 7.10 (1H, dd, *J* 8.3, 7.6Hz), 7.21 (1H, dd, *J* 7.3, 0 8Hz), 7.30 (1H, d, *J* 3.2Hz), 7.44 (1H, d, *J* 8.3Hz); δ_C ($CDCl_3$) 12.8, 18.1, 36.4, 42.4, 103 8, 113.5, 121 8, 122.4, 125 4, 131.7, 132.5, 140.6, 170.6; *m/z* 377 (M^+, 100%), 292 (20%), 123 (16%). Found: C, 63 75, H, 8.31; N, 3.55; S, 8.34 $C_{20}H_{31}NO_2SSi$ requires: C, 63.61; H, 8 27; N, 3.71; S, 8 49%.

ii. Arene: 4-iodo-1-triisopropylsilylindole[10f] (701mg, 1.76mmol); tin reagent· methoxycarbonylmethylthiotrimethylstannane (538mg, 2mmol); catalyst – (197mg, 9 7mol%); solvent: – (40ml) The product (8a, E = SCH_2CO_2Me) was obtained as a colourless oil (652mg, 98%), identical with the above material

4–Ethoxycarbonylmethylthio–1–triisopropylsilylindole (8a, E = SCH_2CO_2Et).— Arene. 4-iodo-1-triisopropylsilylindole[25] (340mg, 0 86mmol); tin reagent: ethoxycarbonylmethylthiotributylstannane (260mg, 0.64 mmol), ; catalyst – (83mg, 11mol%); solvent: – (20ml) The product (8a, E = SCH_2CO_2Et) was obtained as a colourless oil (180mg, 70 %); ν_{max} (film) 2949, 2869, 1736, 1467 cm^{-1}; δ_H ($CDCl_3$) 1 05-1.20 (21H, m), 1 68 (3H, septet, *J* 7 7Hz), 3 68 (2H, s), 4 09 (2H, q, *J* 7 1Hz), 6.78 (1H, dd, *J* 3 3, 0 8 Hz), 7 07 (1H, dd, *J* 8.2, 7.7Hz), 7 20 (1H, dd, *J* 7.7, 0.8Hz), 7 27 (1H, d, *J* 3.3Hz), 7.42 (1H, br d, *J* 8 2Hz); *m/z* 391 (M^+, 2%), 196 (87%), 123 (100%), 108 (19%)

3–Acetyl–4–(methoxycarbonylmethylthio)indole (10) — Arene: 3–acetyl–4–iodoindole (9) (910mg, 3 2mmol); tin reagent: methoxycarbonylmethylthiotrimethylstannane (910mg, 3 40 mmol); catalyst – (170mg, 4 6mol% + triphenylphosphine 160mg, 19 mol%); solvent· – dioxan (32ml) The product (10) was obtained as colourless crystals (700mg, 83%), m.p 139-141°C (lit.[25] m p 140–141 5°C); ν_{max} (Nujol) 3117, 1736, 1624 cm^{-1}; δ_H (d_6–acetone) 2.49 (3H, s), 3 66 (3H, s), 3 77 (2H, s), 7 12 (1H, dd, *J* 7 5, 1 6Hz$_7$), 7 18 (1H, t, *J* 7 9Hz), 7 32 (1H, dd, *J* 7 5, 1 2Hz), 8 20 (1H, d, *J* 3 2Hz), 11 04 (1H, br s), δ_C (d_6–acetone) 28 4, 36 4, 52.4, 110 4, 120 4, 120 8, 123 9, 124 5, 131 7, 134 3, 138 6, 171 1, 192 0, *m/z* 263 (M^+, 92%), 189 (100%), 188 (33%), 186 (35%), 175 (31%) 174 (39%), 162 (31%), 160 (42%)

REFERENCES

1 For many examples, see 'The Merck Index'.11th Edn , Ed S. Budavari, Merck and Co , Rahway, N J , U S A, 1989

2 For a general account see· a) J Miller *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam, 1968, for specific examples of thiation see b) S_NAr· D Landini, F. Montanari and F. Rolla, *J Org. Chem.*, **1983**, *48*, 604, c) S_N1. J D Baleja, *Synth Comm.*, **1984**, *14*, 215; d) S_EAr. : e) benzyne. R.B Bates and K.D Janda, *J Org. Chem* , **1982**, *47*, 4374; f) quinone addition: E.L. McInnis, B. Grant and E Arcelo, *Tetrahedron Lett* , **1981**, *22*, 3807; g) $S_{RN}1$. R Beugelmans, M. Bois-Choisy and B Boudet, *Tetrahedron*, **1983**, *39*, 4153; h) radical· T Fujisawa and T Kojima, *Bull Chem. Soc Jpn* , **1977**, *50*, 1298; i) palladium catalysed: M Kosugi, T. Shimizu and T Migita, *Chem. Lett* , **1978**, 13

3 R Adams and A Ferretti, *J Am Chem Soc.*, **1959**, *81*, 4927.

4 a) B Nicholls and M Whiting, *J. Chem Soc* , **1959**, 551; b) M F Semmelhack, G.R Clark,

J.L Garcia, J.J. Harrison, Y. Thebtaranonth, W.D Wulff and Y Yamashita, *Tetrahedron*, **1981**, *37*, 3957; c) F. Rose-Munch, E Rose, A. Semra, L. Mignon, J. Garcia Oricain and C Knobler, *J Organomet. Chem.*, **1989**, *363*, 297

5 a) J.P. Gilday and D A Widdowson, *Tetrahedron Lett.*, **1986**, 5525; b) D.A. Widdowson, *Phil Trans. R. Soc. Lond.* A, **1988**, *326*, 595.

6 a) A. Alemagna, P. Cremonesi, P Del Buttero, E. Licandro and S. Maiorano, *J. Org. Chem*, **1983**, *48*, 605; b) *ibid.* 3114; c) C. Baldoli, P Del Buttero, S. Maiorano and A. Papagni, *J. Chem. Soc, Chem. Commun.*, **1985**, 1181.

7 S.J. Rosca and S. Rosca, *Rev. Chim.(Bucharest)*, **1974**, *25*, 461

8 R J Card and W. S. Trahanovsky, *J Org. Chem*, **1980**, *45*, 2555

9 R J. Card and W. S Trahanovsky, *J. Org. Chem*, **1980**, *45*, 2560

10 a) M.F. Semmelhack, J Bisaha and M. Czarny, *J Am. Chem. Soc.*, **1979**, *101*, 768; b) M Uemura, N Nishikawa and Y. Hayashi, *Tetrahedron Lett*, **1980**, *21*, 2069; c) M Fukui, T. Ikeda and T Oishi, *Tetrahedron Lett.*, **1982**, *23*, 1605; d) N F Masters and D A Widdowson, *J. Chem. Soc., Chem. Commun*, **1983**, 3065; e) M Uemura, K Take, K. Isobe, T Minami, and Y Hayashi, *Tetrahedron*, **1985**, *41*, 5771, f) P J Beswick, C S Greenwood, T J Mowlem, G Nechvatal and D.A Widdowson, *Tetrahedron*, **1988**, *44*, 7325; g) N F Masters, N Mathews, G Nechvatal and D A Widdowson, *Tetrahedron*, **1989**, *45*, 5755.

11 D N Harpp, T Aida, J. Decesare, C P. Tisnes and T H Chan, *Synthesis*, **1984**, 1037, and references there cited

12 M F Semmelhack and A. Zask, *J. Am. Chem Soc*, **1983**, *105*, 2034

13 For an extensive account, see R F Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, 1985, pp 179-321

14 W J Scott, *J. Chem Soc, Chem Commun*, **1987**, 1755

15 a) S Murahashi, M Yamamura, K Yanagesawa, M Mita and K Kondo, *J. Org Chem.*, **1979**, *44*, 2408, b) T Migita, T Shimizu, Y Asami, J Shiobara, Y Kato and M. Kosugi, *Bull Chem Soc Jpn*, **1980**, *53*, 1385.

16 M. Kosugi, T Ogata, M Terada, H Samo and T Migita, *Bull Chem. Soc Jpn*, **1985**, *58*, 3657

17 D A Widdowson and Y Z Zhang, *Tetrahedron*, **1986**, *42*, 2111

18 C A L Mahaffy and P L Pauson, *Inorg. Synth*, **1979**, *19*, 154

19 J P Gilday, PhD Thesis, London, 1986

20 J R Beck, *J Heterocyclic Chem*, **1978**, *15*, 513

21 Symmetrical disulpides C N Yiannios and J V Karabinos, *J Org Chem*, **1963**, *28*, 3246 Sulphur transfer agents D N Harpp, K. Steliou and T H Chan,*J Am Chem Soc*, **1978**, *100*, 1222 and references there cited

22 G Nechvatal and D A Widdowson, *J Chem Soc, Chem Commun*, **1982**, 467.

23 Alkylthiostannanes were made according to ref 11

24 P Manya, A Sekera and P Rumpf, *Tetrahedron*, **1970**, *26*, 467

25 A P Kozikowski, M N Greco and J P Springer, *J. Am Chem Soc*, **1982**, *104*, 7622