Palladium- and cobalt-mediated cyclisations of halo-polyenes: a comparative study

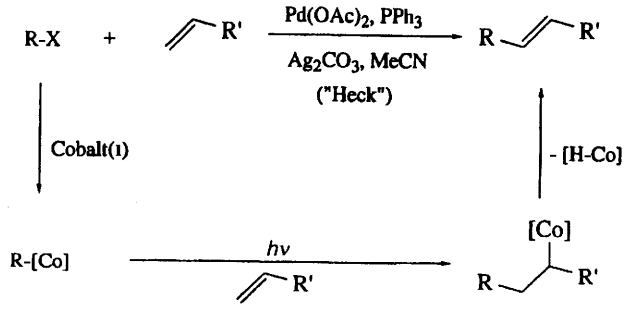
Amjad Ali, G. Bryon Gill, Gerald Pattenden,* Graeme A. Roan and Toh-Seok Kam

Department of Chemistry, Nottingham University, Nottingham NG7 2RD, UK

Cobalt(I)-mediated mono- and bi-cyclisations of halo-polyenes are compared and contrasted with corresponding reactions using the Heck reaction. The procedures are found to complement one another, with each having advantages and disadvantages, in the cases studied. Thus, treatment of the vinyl iodide 1 under Heck conditions led to the novel 1,3-diene 3 in 93% yield, whereas reaction between 1 and cobalt(I) salophen resulted in the formation of the organocobalt complex 4 (~ 50%) as black crystals. Subsequent irradiation of 4 then led to the 6,5-ring fused bicycle 5 in 85% yield. In similar fashion, a Heck reaction with the analogous vinyl iodide 8 produced the product 9 of 6-ring cyclisation followed by β-hydride elimination, whereas the corresponding cobalt-mediated reaction with 8 led to the new organocobalt 10 albeit in only low yield (~ 20%). In reactions akin to those studied by Overman *et al.*, Heck reaction with the dienyl aryl iodide 14 was shown to lead to a mixture of the bicycle 16 and the tricycle 17 in a 1 : 1 ratio. By contrast treatment of 14 with cobalt(I) salophen produced largely the tetralin 18. The iodo-diene 33 gave rise to the spirocycle 35 under Heck reaction conditions, and the related spirocycle 42 was produced from the bromo-acetal 40 *via* 41, using cobalt(I) mediated reactions.

The palladium-catalysed coupling reaction between alkenes and haloalkenes or haloarenes, *i.e.* the Heck reaction,[1] has become one of the most revered reactions for the synthesis of carbon-to-carbon bonds in recent years. Examples of its applications in synthesis abound in the contemporary literature.[2] The Heck reaction can be conducted in both intermolecular and intramolecular modes; cascade processes are becoming commonplace and enantioselective constructions are possible. Taken together with several mechanistically related palladium-catalysed reactions,[3] the Heck reaction and variants are now a first choice option for synthetic chemists in all types of carbon-to-carbon bond forming reactions. An organometallic reaction which shows a close homology to the Heck reaction is the cobalt(I)-mediated reaction between alkenes and organic halides, *cf.* Scheme 1. During the late 1980s we recognised the scope for these cobalt(I)-mediated radical-based reactions in synthesis and developed a variety of protocols for the elaboration of a range of fused-ring carbo- and hetero-cycles and functional group manipulations, involving alkyl, vinyl, acyl and carbonyl organocobalt precursor molecules.[4,5] Although the similarity between the Heck reaction and these cobalt(I)-mediated reactions is somewhat opaque, since they operate by significantly different mechanisms, a direct comparison of their scope in synthesis, particularly in ring constructions, from identical precursor molecules seemed warranted. Accordingly we have carried out a comparative study of the complementary palladium catalysed and cobalt(I)-mediated intramolecular cyclisation reactions of a range of alkyl, vinyl and aryl halides bearing proximate alkene double bonds. The outcome of this investigation is summarised in this paper.

We first compared the Heck and the cobalt(I)-mediated reactions with the substituted vinyl iodide **1** which was easily assembled from (±)-linalool and methoxyallene in the presence of *N*-iodosuccinimide.[6] Thus, treatment of **1** with 1 mol% $Pd(OAc)_2$ in the presence of PPh_3 (4 mol %) and an equivalent of Ag_2CO_3 at room temperature for 10 h led to a single product in 93% yield, whose spectroscopic data showed that it corresponded to the novel 1,3-diene **3**. Significantly, no bicyclic product, *viz.* **5**, produced as a result of insertion of the σ-alkylpalladium intermediate **2** into the proximal trisubstituted

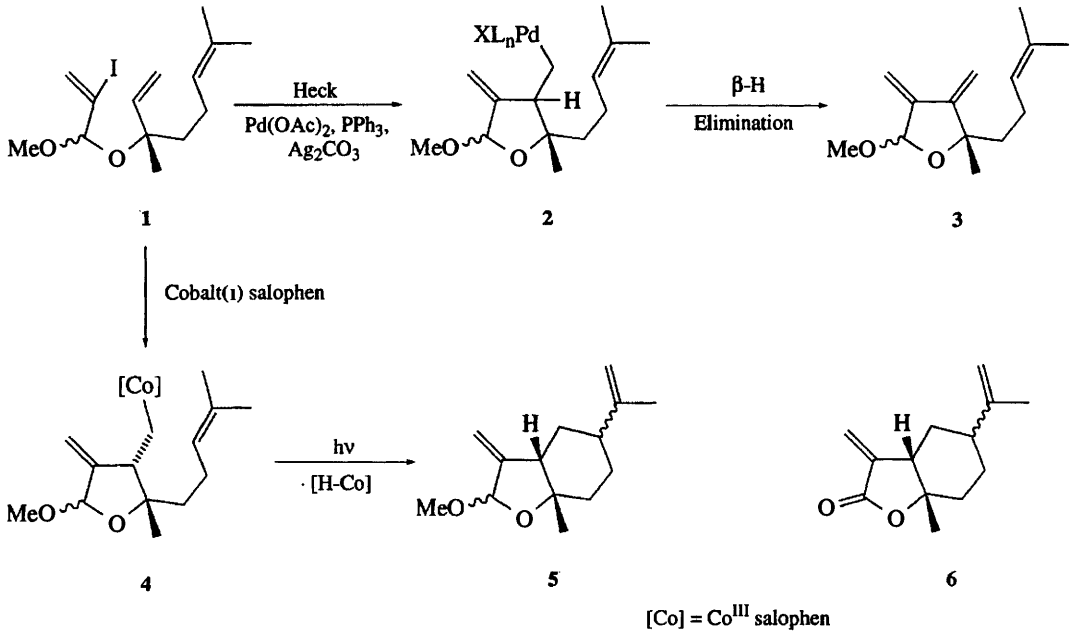


[Co] = Co^{III} salophen

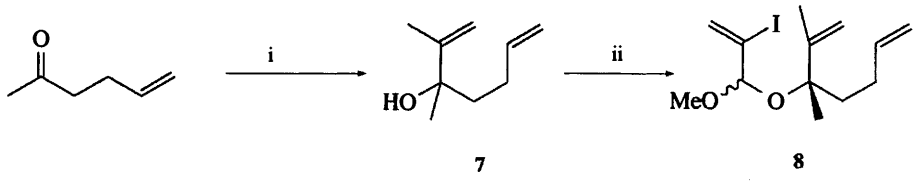
Scheme 1

double bond, was intercepted in this reaction; instead the intermediate **2** decomposed to **3** by straightforward β-hydride elimination. By contrast, reaction between the vinyl iodide **1** and cobalt(I) salophen (generated from Co^{II} salophen and 1% NaHg), led to the air-sensitive organocobalt complex **4** (~ 50%) as black crystals, mp 102–104 °C, with no detectable evidence for the co-formation of the product **5** resulting from cyclisation and β-hydride elimination in **4**.[6] However, when a solution of the organocobalt **4** was irradiated using light from a conventional ultraviolet sunlamp, it underwent facile carbon-to-cobalt bond homolysis, followed by 6-*exo*-trig cyclisation of the resulting carbon-centred radical onto the adjacent double bond and β-hydride elimination producing the 6,5-ring fused bicycle **5** in 85% yield. Oxidation of **5** using Jones' reagent then led to the corresponding lactone **6** (Scheme 2).

We next examined the palladium and cobalt organometallic chemistry of the analogous vinyl iodide **8**, in Scheme 3, containing an additional methyl group on the alkene bond adjacent to the vinyl iodide residue. We envisaged that this substitution pattern would preclude β-hydride elimination from the product **11** resulting from any initial 5-ring cyclisation process, *cf.* **2** and **11**; in this manner we hoped to access the bicyclic acetal **12** from these reactions. Much to our chagrin, however, reaction between the vinyl iodide **8** and $Pd(OAc)_2$–



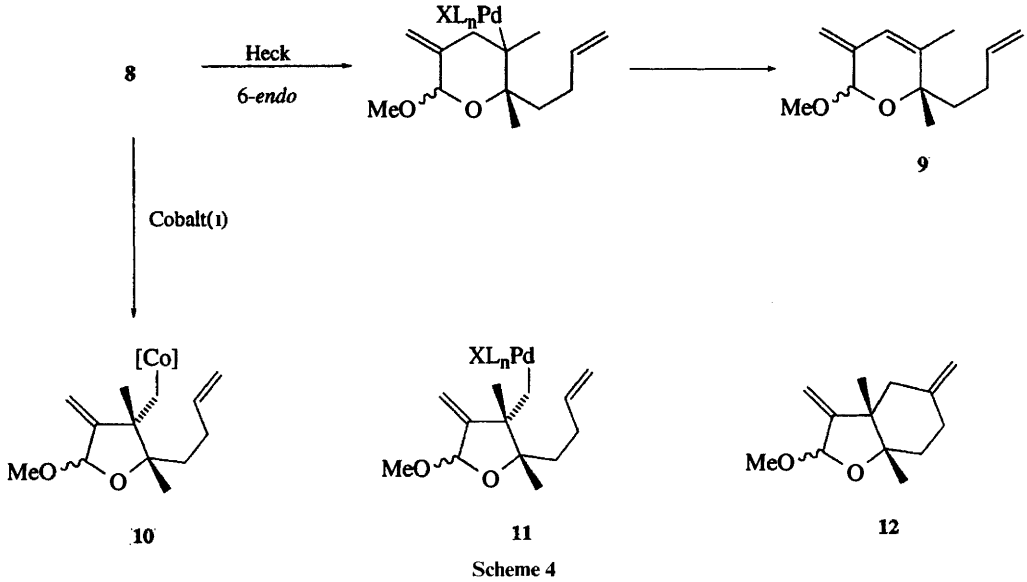
Scheme 2



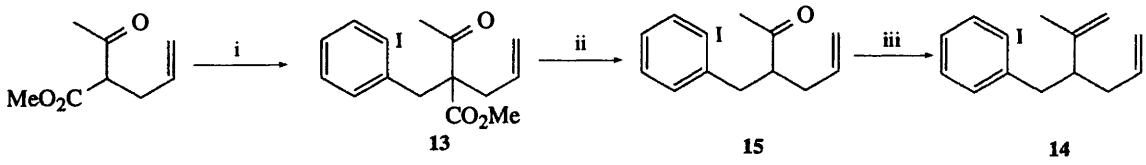
Scheme 3 *Reagents:* i, Mg, 2-bromopropene; ii, methoxyallene, *N*-iodosuccinimide, CCl_4

PPh_3–Ag_2CO_3 instead led to only the product **9** of 6-ring cyclisation followed by β-hydride elimination in 62% yield (Scheme 4). In addition, treatment of **8** with cobalt(I) salophen led only to the highly unstable organocobalt complex **10**, in low yield (~ 20%), together with substantial amounts of recovered starting material. Tertiary carbon substituted organocobalt reagents/intermediates are not known, and the low yield of **10** observed in the cobalt(I) mediated reaction with **8** no doubt reflects the severe steric congestion felt by the quaternary centres in **10** and intermediates leading to it from the starting material.

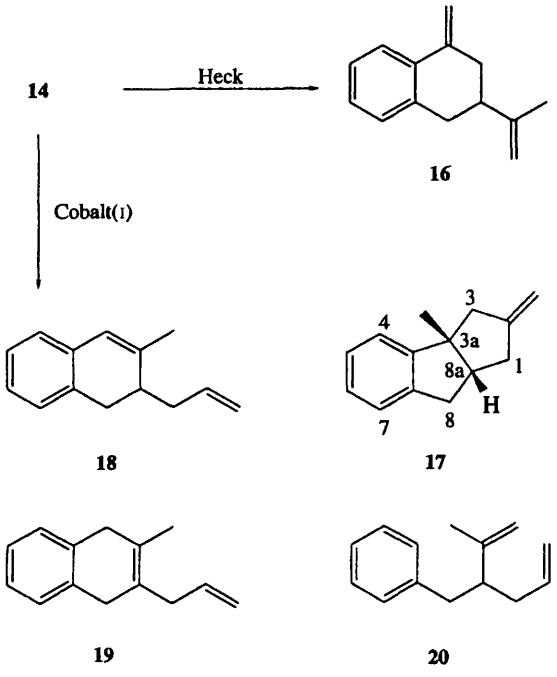
Heck reactions with *ortho*-diene substituted aryl iodides have been described earlier by Overman *et al.*,[7] and we felt it would be prudent to compare some of these reactions with the corresponding cobalt(I) mediated processes. Thus, we first prepared the dienyl aryl iodide **14** as shown in Scheme 5.



Scheme 4



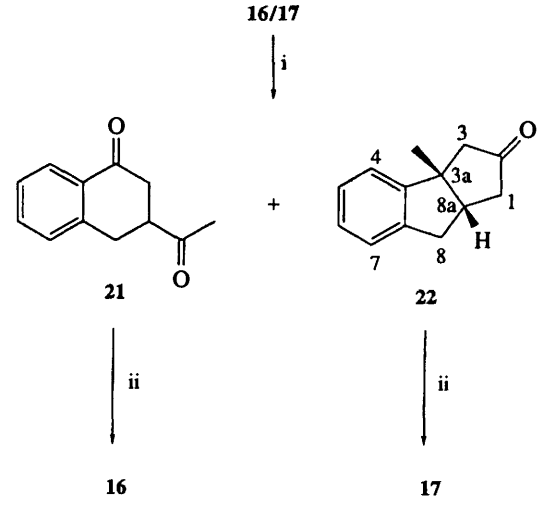
Scheme 5 *Reagents:* i, NaH, 2-iodobenzyl chloride; ii, LiCl, DMSO, H_2O, 150 °C; iii, methyltriphenylphosphonium bromide, KOBu^t



Scheme 6

Overman *et al.* had shown that cyclisation of this dienyl aryl iodide under Heck reaction conditions leads to the bicycle **16** and the tricycle **17** in a 3 : 2 ratio (Scheme 6). We have confirmed this outcome. By contrast, we found that treatment of **14** with cobalt(I) salophen results in a more selective cyclisation and produces largely the tetralin **18**, contaminated by a small amount of the corresponding $\Delta^{2,3}$-alkene isomer **19**; the formation of **18** was also accompanied by ~ 10% of the product of reduction (de-iodination) of **14**, namely **20**.

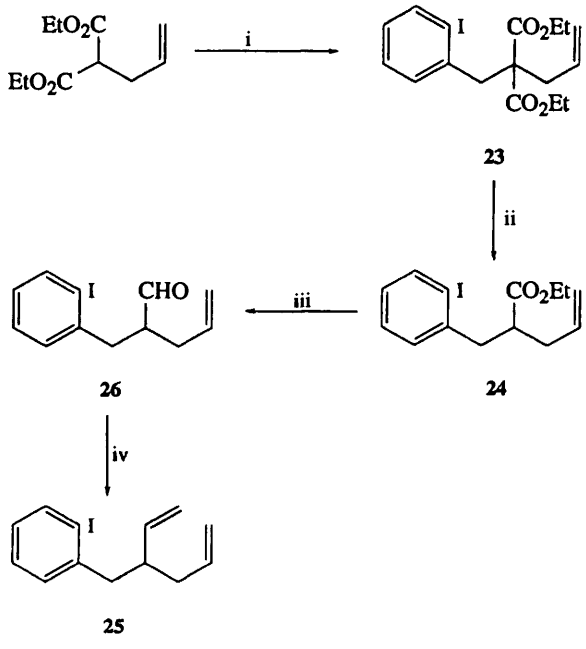
The isomeric alkenes **16** and **17** were inseparable by normal chromatographic methods and so chemical means were employed to confirm their structures. Thus, oxidative cleavage of the mixture of **16** and **17** using osmium tetroxide and potassium periodate[8] first gave the diketone **21** and the ketone **22** which could be easily separated from each other by routine chromatography. The *cis* nature of the ring junction in **22** was assigned unambiguously from H,H and H,C COSY NMR studies. Wittig methylenation reactions with the separated ketones **21** and **22** then reconstituted the pure alkenes **16** and **17** respectively (Scheme 7).



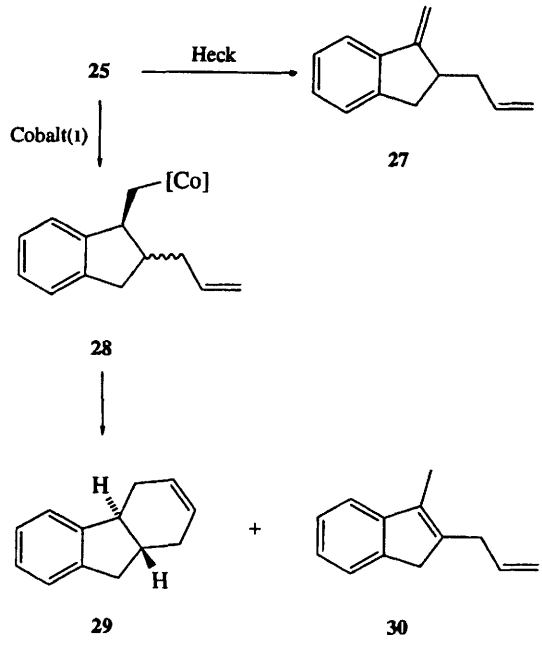
Scheme 7 *Reagents:* i, OsO_4, KIO_4; ii, methyltriphenylphosphonium bromide, KOBu^t

We next studied the homologue **25** of **14** which was prepared in a straightforward manner as outlined in Scheme 8. In somewhat similar fashion to the outcomes of treatments of the vinyl iodide **1** with palladium and cobalt reagents, cyclisation of **25** under Heck reaction conditions led exclusively to the 1,5-diene **27** (67%), whereas the corresponding reaction with cobalt(I) salophen produced the organocobalt complex **28** as a black solid in 66% yield (Scheme 9). Subsequent irradiation of a solution of **28** in benzene with a 300 W sunlamp led to a 2 : 1 mixture of the product **30** of dehydrocobaltation, and the fluorene product **29** of further cyclisation from **23** followed by dehydrocobaltation.

Finally, in our studies with diene substituted aryl iodides we prepared the 1,5-diene **33**, as illustrated in Scheme 10. Similar to Overman *et al.*, we found that a Heck reaction with the iodo-diene **33** provided a concise synthesis of the spirocycle **35** in

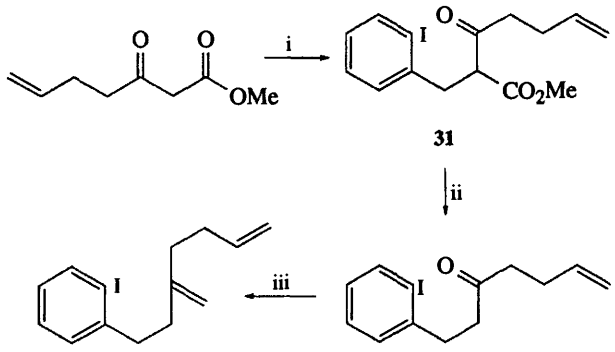


Scheme 8 *Reagents:* i, NaH, 2-iodobenzyl chloride; ii, LiCl, DMSO, H_2O, 150 °C; iii, DIBAL-H, −78 °C; iv, methyltriphenylphosphonium bromide, KOBu^t



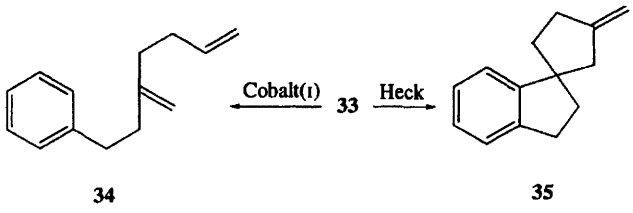
[Co] = Co^{III} salophen

Scheme 9



Scheme 10 *Reagents:* i, NaH, 2-iodobenzyl chloride; ii, NaOH (5 mol dm^{-3}), reflux; iii, methyltriphenylphosphonium bromide, $KOBu^t$

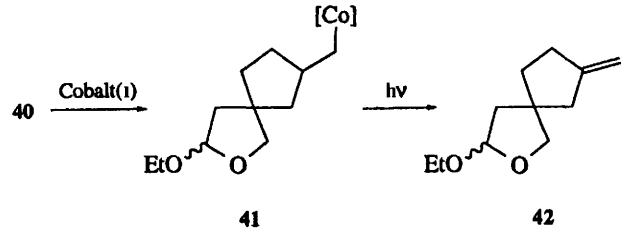
> 80% yield (Scheme 11). Disappointingly, however, treatment of **33** with cobalt(I) salophen led to only the product **34** of de-iodoination.



Scheme 11

In our studies of the comparative chemistry of organic halides with palladium and cobalt reagents we finally examined the alkyl halide **40**, which was prepared from hex-5-en-2-one as shown in Scheme 12. Not unexpectedly, treatment of this alkyl halide under Heck reaction conditions left the starting material unchanged. Gratifyingly, however, reaction of **40** with cobalt(I) oxime resulted in a clean bicyclisation producing the spirocyclic cobalt(III) oxime **41** as a stable orange powder in 47% yield (Scheme 13). Dehydrocobaltation of **41**, using a sunlamp, then produced the corresponding alkene **42** as a colourless oil in 65% yield.

The above results highlight a number of similarities between the Heck reaction and cobalt(I) mediated reactions involving organic halides and alkenes. In some respects the procedures nicely complement each other but in other respects there are marked differences. Thus, the cobalt(I) chemistry is embroiled in electron transfer processes and free radical intermediates, whereas nucleophilic Pd^0 is implicated in the Heck reaction. The palladium reactions are catalytic whereas stoichiometric amounts of cobalt(I) reagents are generally needed.[9] The Heck reaction appears to be better suited to the elaboration of quaternary carbon centres and to hindered transition states. Cobalt(I) reagents are suitable for use with alkyl halides as well



$[Co] = Co^{III}(dmgH)_2py$

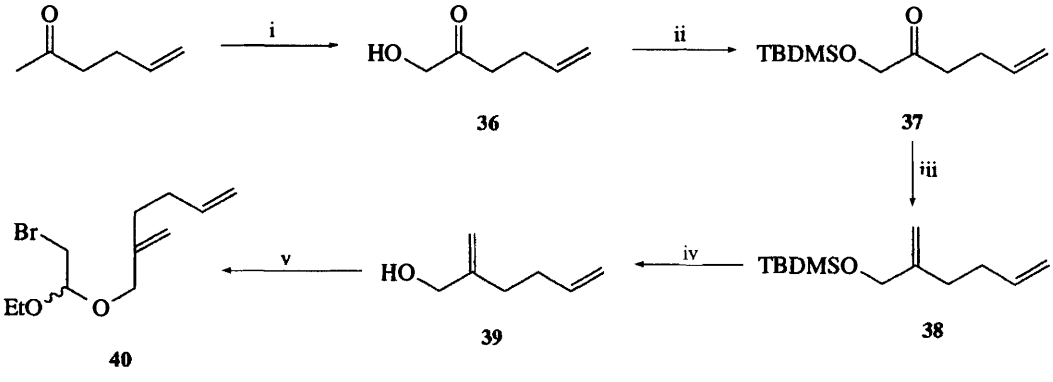
Scheme 13

as vinyl and aryl; this is not the case with the Heck reaction. In addition, organocobalt intermediates and reagents can frequently be intercepted in cobalt(I) mediated reactions. By contrast, premature β-hydride elimination can present limitations in synthesis using the Heck reaction.

Experimental

General details

Melting point determinations were made on a Reichert Kofler micro hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1720 or 1600 Series FTIR spectrometer and were calibrated using a standard polystyrene film; the spectra were recorded as thin films (for liquids) or in chloroform solutions (for solids). UV–VIS spectra were recorded as solutions in spectroscopic grade ethanol using a Philips PU 8720 or a Perkin-Elmer Lambda 16 spectrophotometer. Unless stated otherwise, solutions in deuteriochloroform were used for the determination of NMR spectra. Shifts are expressed in ppm downfield from Me_4Si as internal standard. The ^1H and ^{13}C NMR spectra were recorded on a 270 MHz JEOL EX-270, 80 MHz Bruker WP80SY, 250 MHz Bruker WM250 or a 400 MHz Bruker AM400 instrument. Signals were singlets unless specified otherwise: *i.e.* d = doublet, dd = double doublet, ddd = double doublet of doublets, dt = double triplet, q = quartet, quint. = quintet, m = multiplet, br = broad. *J* values are given in Hz. Assignments in the ^1H spectra were consistent with signal intensities, and in the ^{13}C spectra with the results of the DEPT pulse sequence. Assignments were supported by 2D H–H and H–C COSY experiments where necessary. The 2-iodobenzyl alkenes **13–15**, **23–26** and **31–33** exhibited complicated NMR spectra. This complexity cannot be due simply to the presence of chiral centres in the molecules since **23**, **32** and **33** are formally symmetrical molecules. It appears that rotation about the Ar–CH_2 bond is somewhat hindered in these systems. Mass spectra were recorded on an AEI MS-902 or an MM-701CF instrument, using electron impact ionisation at 70 eV unless stated otherwise. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser.



Scheme 12 *Reagents:* i, LDA,TMSCl, H_2O quench; MCPBA then HCl; ii, TBDMSCl, imidazole; iii,methyltriphenylphosphonium bromide, $KOBu^t$; iv, TBAF; v, NBS, ethyl vinyl ether

Flash chromatography was performed using Merck silica gel 60, and all solvents were redistilled before use. 'Ether' refers to diethyl ether, and light petroleum refers to the fraction bp 40–60 °C. All reactions were monitored by TLC using Merck silica gel 60 F254 precoated aluminium plates. Organic extracts were dried over anhydrous magnesium sulfate prior to removal using a Büchi rotary evaporator. Irradiations of organocobalt compounds were performed using an external Philips Ultraphil type KL 2866 (300 W) health lamp and standard Pyrex apparatus.

N,N'-o-Phenylenebis(salicylideaminato)cobalt(II) [10] [salophencobalt(II)]†

A flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (18.08 g, 72.6 mmol) in propanol (690 cm^3) was purged with nitrogen, and then warmed to 50 °C under a nitrogen atmosphere. *N,N'*-Bis(salicylidene)-*o*-phenylenediamine (22.5 g, 71.7 mmol) was added in one portion, and the resulting black suspension was then stirred and heated under reflux under a nitrogen atmosphere for 6 h. The mixture was then cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give black crystalline cobalt(II) salophen (28.1 g, 100%).

Sodium salophencobaltate(I) [sodium cobalt(I)salophen] [11]

Mercury (40 g, 0.2 mol) was added with care to freshly cut small pieces of sodium (0.4 g, 17.7 mmol) under a flow of nitrogen. The reaction flask was swirled vigorously until an exothermic reaction was observed; slight warming with a Bunsen flame was occasionally necessary to initiate the reaction. The 1% sodium amalgam thus formed was allowed to cool to room temperature under nitrogen, and then added to a stirred and deoxygenated solution of salophencobalt(II) (1.49 g, 4.0 mmol) in dry tetrahydrofuran (THF) (200 cm^3) at room temperature under an atmosphere of argon. The mixture was stirred for 1.5 h in the dark under argon and then allowed to settle during 0.5 h. About 90% of the dark green solution of the title compound was then transferred, using a cannula, into a dry argon-flushed flask. This material was used immediately.

3,7-Dimethyl-3-(1-methoxy-2-iodoprop-2-enoxy)octa-1,6-diene 1

A solution of methoxyallene [12] (1.0 g, 14.28 mmol) and (±)-linalool (2.64 g, 17.14 mmol) in tetrachloromethane (20 cm^3) was added dropwise over 3 min to a stirred and cooled (0 °C) suspension of *N*-iodosuccinimide (3.21 g, 14.28 mmol) in tetrachloromethane (20 cm^3) under an atmosphere of nitrogen. The suspension was filtered and the solvent was then removed from the filtrate by evaporation under reduced pressure to leave a colourless liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:10) to give the *iodoacetal* **1** (2.54 g, 51%) a *ca.* 1:1 mixture of diastereoisomers, as a colourless oil; ν_{max}/cm^{-1} (film) 3086, 2972, 2930, 2827, 1741, 1616, 1450, 1413, 1376, 1240, 1202, 1074, 1051, 919 and 837; δ_H(270 MHz) 6.54 (1 H, d, *J* 1, CH*H*=CI), 6.00 (1 H, d, *J* 1, C*H*H=CI), 5.92 (0.5 H, dd, *J* 17.2 and 10.9, C*H*=CH_2), 5.82 (0.5 H, dd, *J* 17.2 and 11.2, C*H*=CH_2), 5.22–5.15 (2 H, m, CH=CH_2), 5.11–5.06 (1 H, m, C*H*=CMe_2), 4.62 (0.5 H, s, C*H*OMe), 4.57 (0.5 H, s, C*H*OMe), 3.20 (1.5 H, s, OCH_3), 3.17 (1.5 H, s, OCH_3), 2.08–1.98 (2 H, m, =CHCH_2), 1.67 (3 H, s, =CCH_3), 1.59 (3 H, s, =CCH_3), 1.64–1.56 (2 H, m, CH_2), 1.36 (1.5 H, s, CH_3) and 1.29 (1.5 H, s, CH_3); δ_C(68 MHz) 142.9 and 142.4 (*C*H=CH_2), 131.8 (=*C*Me_2), 127.9 and 127.7 (IC=*C*H_2), 124.5 (*C*H=CMe_2), 115.7 and 115.1 (CH=*C*H_2), 111.2 and 110.7 (IC=CH_2), 99.5 and 99.4 (*C*HO_2), 80.0 and 79.7 (O*C*Me), 51.8 and 50.9 (O*C*H_3), 41.9 and 41.0 (CH_2CH_2*C*H=), 26.0 (*C*H_3), 23.0 (*C*H_3), 22.9 (*C*H_3), 22.8$_2$ and 22.7$_7$ (CH_2*C*H_2CH=) and 17.9 (*C*H_3); *m/z* 153.1296 (9%) (*M* − C_4H_6OI, $C_{10}H_{17}O$ requires 153.1279), 137 (5), 136 (15), 121 (12), 93 (47), 92 (11), 83 (50), 81 (20), 80 (26) and 71 (43).

3,4-Dimethylidene-2-methoxy-5-methyl-5-(4-methylpent-3-enyl)tetrahydrofuran 3

A solution of the vinyl iodide **1** (0.200 g, 0.57 mmol), palladium(II) acetate (1.3 mg, 1 mol %), triphenylphosphine (6.0 mg, 4 mol %) and silver(II) carbonate (0.157 g, 0.57 mmol) in dry acetonitrile (10 cm^3) was stirred at room temperature for 10 h under an atmosphere of nitrogen. The resulting mixture was filtered through Celite and evaporated to dryness under reduced pressure to leave a brown residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (pentane) to give the *triene* **3** (0.123 g, 93%), a *ca.* 1:1 mixture of diastercoisomers, as a clear oil; ν_{max}/cm^{-1} (film) 3084, 2970, 2927, 2826, 1745, 1632, 1449, 1376, 1188, 1091, 1027, 969 and 901; δ_H(400 MHz) 5.53 [0.5 H, d, *J* 1.5, *H*HC(a)=], 5.50 [0.5 H, d, *J* 1.3, *H*HC(a)=], 5.41 [0.5 H, s, *H*HC(b)=], 5.37 [0.5 H, s, *H*HC(b)=], 5.26–5.24 [2 × 0.5 H, m, H*H*C(a)=], 5.15 [0.5 H, s, H*H*C(b)=], 5.12 (0.5 H, s, H*H*C(b)=], 5.07–4.99 (1 H, m, C*H*=CMe_2), 4.77 and 4.76 (2 × 0.5 H, 2 × s, C*H*OMe), 3.38 and 3.34 (2 × 1.5 H, 2 × s, OCH_3), 1.98 (3 H, s, CH_3), 1.62–1.48 (4 H, m, CH_2CH_2), 1.54 and 1.50 (2 × 1.5 H, 2 × s, CH_3) and 1.35 and 1.26 (2 × 1.5 H, 2 × s, CH_3); δ_C(100 MHz) 150.7 and 149.9 [*C*(a)=CH_2], 146.2 and 145.8 [*C*(b)=CH_2], 131.5$_2$ and 131.4$_7$ (=*C*Me_2), 124.4$_2$ and 124.3$_8$ (*C*H=CMe_2), 108.6 and 108.0 [C(a)=CH_2], 104.3 and 104.2 (*C*HO_2), 103.8 and 103.7 [C(b)=*C*H_2], 86.7 and 86.6 (O*C*Me), 54.9 and 54.1 (O*C*H_3), 42.4 and 41.9 (*C*H_2CH_2CH=), 29.4 (*C*H_3), 26.4 (*C*H_3), 25.7 (*C*H_3), 23.0 and 22.5 (CH_2*C*H_2CH=), 21.1 (*C*H_3), 17.7 (*C*H_3); *m/z* 222.1614 (5%) (*M*, $C_{14}H_{22}O_2$ requires 222.1620), 207 (13), 190 (15), 175 (8), 162 (6), 151 (6), 147 (15), 140 (24) and 139 (100).

5-Methyl-5-(4-methylpent-3-enyl)-3-methylidene-2-methoxytetrahydrofuran-4-ylmethyl[cobalt(III)salophen] 4

A solution of the iodoacetal **1** (0.350 g, 1.0 mmol) in dry deoxygenated tetrahydrofuran (THF, 5 cm^3) was added dropwise over 1 min by means of a syringe, to a stirred green solution of sodium cobalt(I) salophen (0.745 g, 2.0 mmol) in dry deoxygenated THF (120 cm^3) in the dark and under an atmosphere of nitrogen. The resulting mixture was stirred for 3 h in the dark under nitrogen, and then filtered at reduced pressure in the dark to leave a brown crystalline residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel in the dark (methanol–chloroform, 1:10) to give the *cobalt salophen* **4** (280 mg, 47%), a *ca.* 1:1 mixture of diastereoisomers, as a black solid mp > 102–103 °C dec.; ν_{max}/cm^{-1} ($CHCl_3$) 3040, 2920, 1625, 1610, 1430 and 900; δ_H(270 MHz) 8.75 and 8.73 (2 × 1 H, 2 × s, 2 × *HC*=N), 7.98–7.86 (2 H, m, 2 × Ar*H*), 7.48–7.14 (8 H, m, 8 × Ar*H*), 6.72–6.64 (2 H, m, 2 × Ar*H*), 5.13 and 5.12 (2 × 0.5 H, 2 × s, C*H*OMe), 4.93–4.81 (2 H, m, CH_2=C), 4.78 [1 H, m, C*H*=C$(CH_3)_2$], 3.31–3.25 (2 H, m, CH_2Co), 2.81 (3 H, s, OCH_3), 1.82 (3 H, s, CH_3), 1.65 (3 H, s, CH_3), 1.51–0.82 (4 H, m, 2 × CH_2) and 0.64 (3 H, s, CH_3); δ_C(68 MHz), 168.2 and 168.0 (=*C*–), 155.9 (=*C*H), 149.6 (=*C*–), 144.2 and 144.0 (=*C*–), 135.2 (=*C*H), 134.6 (=*C*H), 134.5 (=*C*H), 134.0 (=*C*H), 133.6 (=*C*H), 131.2 (=*C*–), 127.0 (=*C*H), 124.7 and 124.6 (2 × =*C*H), 119.5 (=*C*–), 116.5 and 116.4 (2 × =*C*H), 114.8 (=*C*H), 110.2 (=*C*H_2), 102.7 (*C*H=CMe_2), 81.9 (O*C*Me), 51.4 and 50.8 (O*C*H_3), 39.6 (*C*H_2), 25.7 (*C*H_3), 21.9 (*C*H_2), 21.7 (*C*H_3) and 17.8 (*C*H_3); *m/z* (FAB) 595 (*M* − C_2H_7), 481, 360 and 278.

8-Methoxy-6-methyl-3-(1-methylethenyl)-9-methylidene-7-oxabicyclo[4.3.0]nonane 5

Dry nitrogen gas was bubbled through dry benzene (70 cm^3) for 1 h. The salophen complex **4** (0.280 g, 0.44 mmol) was added

† For convenience, hereafter the abbreviation salophen is used to refer to the coordinated ligand *N,N'-o*-phenylenebis(salicylideaminato).

and the red solution which formed was then photolysed for 19 h under an atmosphere of nitrogen. The resulting mixture was evaporated under reduced pressure to leave a black solid residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (methanol–chloroform, 1:10) to give the *bicyclic acetal* **5** (86 mg, 50%), a mixture of diastereoisomers, as a pale yellow oil; ν_{max}(film)/cm^{-1} 2900 br, 1645, 1448 br, 1374, 1104, 1043, 978 and 888; δ_H(270 MHz) 5.19 and 5.15 (1 H, 2 × s, C*H*OMe), 5.01, 4.95, 4.92 and 4.88 (2 H, 4 × s, CH_2=C), 4.73, 4.69, 4.68 and 4.61 (2 H, 4 × s, CH_3C=CH_2), 3.50, 3.46 and 3.41 (3 H, 3 × s, OCH_3), 2.71–1.20 (8 H, complex series of m, 3 × CH_2 and 2 × C*H*), 1.74 and 1.66 (3 H, 2 × s, CH_3) and 1.40 and 1.32 (3 H, 2 × s, CH_3); δ_C(68 MHz) 146.6, 144.6, 144.4 and 141.3 (2 × quat. =*C*–), 111.4, 110.4, 109.1 and 108.6 (2 × =CH_2), 100.4 and 98.0 (*C*HO_2), 83.2 and 82.3 (O*C*Me), 55.8, 55.1 and 54.7 (O*C*H_3), 49.6, 49.2, 47.9, 47.5 and 43.2 (2 × *C*H), 42.1, 39.9, 37.2, 35.5, 30.4, 28.1, 26.8, 25.7 and 24.3 (3 × *C*H_2) and 29.0, 23.7, 21.9, 19.4 and 15.4 (2 × CH_3); *m/z* 222.1630 (2%) (*M*, $C_{14}H_{22}O_2$ requires 222.1620), 191 (3), 167 (40), 163 (15), 149 (100), 113 (24), 112 (14) and 83 (22).

6-Methyl-3-(1-methylethenyl)-9-methylidene-7-oxabicyclo-[4.3.0]nonan-3-one 6

A solution of Jones' reagent (0.10 cm^3, 0.18 mmol) [from the addition of chromium trioxide (0.85 g) to water (1.5 cm^3) and concentrated sulfuric acid (0.75 cm^3)] was added over 3 min to a stirred and cooled (0 °C) solution of the acetal **5** (77 mg, 0.36 mmol) in dry acetone (8 cm^3) under an atmosphere of nitrogen. The resulting solution was allowed to warm to ambient temperature and then stirred for 1 h under nitrogen. Isopropyl alcohol (1.0 cm^3) was added dropwise to the suspension and the solvent was then removed from the resulting mixture by evaporation at reduced pressure. The orange solid thus obtained was adsorbed onto silica gel and then purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:4) to give the *lactone* **6** (16 mg, 42%), a mixture of diastereoisomers, as a clear oil; ν_{max}/cm^{-1} (film) 3450, 2927, 2855, 1767, 1715, 1645, 1455, 1379, 1261, 1175, 1123, 1104, 937 and 891; δ_H(400 MHz) 6.16 and 6.11 (1 H, 2 × s, *syn*-OC–C=C*H*H), 5.54 and 5.46 (1 H, 2 × s *anti*-OC–C=CH*H*), 4.79, 4.76, 4.71 and 4.68 (2 H, 4 × s, MeC=CH_2), 2.74–2.62 (1 H, m, C*H*), 2.37–2.17 (2 H, m), 2.05–1.40 (6 H, complex series of m), 1.31 (3 H, s, CH_3) and 1.26 (3 H, s, CH_3); *m/z* 191.1078 (2) (*M* − Me, $C_{12}H_{15}O_2$ requires 191.1072), 162 (2), 161 (3), 147 (9), 145 (4) and 125 (12).

2,3-Dimethylhepta-1,6-dien-3-ol 7

A solution of 2-bromopropene (4.0 g, 33.06 mmol) in dry THF (5 cm^3) was added dropwise over 10 min to a stirred and cooled (0 °C) suspension of anhydrous magnesium turnings (activated with a single crystal of iodine) in dry THF (50 cm^3) under an atmosphere of nitrogen. The resulting suspension was allowed to warm to ambient temperature and then a solution of hex-5-en-2-one (3.09 g, 31.49 mmol) in dry THF (5 cm^3) was added dropwise over 5 min under an atmosphere of nitrogen. The reaction mixture was then stirred for 3 h under nitrogen. The solution was cooled (0 °C) and then saturated aqueous ammonium chloride (10 cm^3) was added. The residue was dissolved in water (60 cm^3) and the resulting aqueous solution was extracted with diethyl ether (75 and 3 × 20 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed by evaporation at reduced pressure to leave a yellow liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:5), to give the *dienol* **7** (4.18 g, 95%) as a colourless oil; ν_{max}/cm^{-1} (film) 3357 br, 2956, 2859, 1472, 1388, 1361, 1256, 1101, 1064, 837, 776 and 735; δ_H(270 MHz) 5.92–5.77 (1 H, ddt, *J* 16.8, 10.2 and 6.6, C*H*=CH$_2$), 5.06–4.85 (4 H, m, 2 × CH=CH_2), 2.04 (3 H, s, CH_3CO), 2.01 (1 H, br s, OH), 1.76 (3 H, s, CH_3C=) and 1.82–1.61 (4 H, br m, 2 × CH_2); δ_C(68 MHz) 150.1 (CH_3C=CH_2), 138.8 (*C*H=CH$_2$), 114.3 (=*C*H$_2$), 109.6 (=CH_2), 75.2 (*C*OH), 39.1 (*C*H$_2$), 28.2 (*C*H$_2$), 27.6 (*C*H$_3$) and 19.3 (*C*H$_3$); *m/z* 122.1113 (1.5%) (*M* − H_2O, C_9H_{14} requires 122.1096), 107 (7), 85 (100), 69 (15), 57 (17) and 43 (96).

2,3-Dimethyl-3-(1-methoxy-2-iodoprop-2-enyloxy)hepta-1,6-diene 8

A solution of methoxyallene (see above) (1.0 g, 14.28 mmol) and 2,3-dimethylhepta-1,6-dien-3-ol (2.40 g, 17.14 mmol) in tetrachloromethane (15 cm^3) was added dropwise over 3 min to a stirred and cooled (0 °C) suspension of *N*-iodosuccinamide (3.86 g, 17.14 mol) in tetrachloromethane (30 cm^3) under an atmosphere of nitrogen. The resulting suspension was allowed to warm to ambient temperature and then stirred for 3 h under an atmosphere of nitrogen. The suspension was filtered and the solvent removed from the filtrate by evaporation at reduced pressure to leave a colourless liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:10) to give the *iodoacetal* **8** (2.08 g, 43%), a *ca.* 1:1 mixture of diastereoisomers, as a colourless oil; ν_{max}/cm^{-1} (film) 3077, 2976, 2950, 2827, 1641, 1615, 1448, 1377, 1202, 1165, 1075, 1044 and 909; δ_H(400 MHz) 6.45 (1 H, s, IC=C*H*H), 5.96 (0.5 H, s, IC=CH*H*), 5.95 (0.5 H, s, IC=CH*H*), 5.80–5.69 (1 H, 2 × ddt, C*H*=CH$_2$), 4.98–4.85 (4 H, m, CH=CH_2 and MeC=CH_2), 4.46 (0.5 H, s, C*H*OMe), 4.45 (0.5 H, s, C*H*OMe), 3.11 (1.5 H, s, OCH_3), 3.08 (1.5 H, s, OCH_3), 2.08–1.86 (2 H, m, CH_2CH=), 1.70 (1.5 H, s, CH_3C=), 1.60 (1.5 H, s, CH_3C=), 1.72–1.57 (2 H, m, CH_2CH$_2$CH=), 1.34 (1.5 H, s, CH_3CO) and 1.26 (1.5 H, s, CH_3CO); δ_H(100 MHz) 146.9 and 146.4 (MeC=), 138.5$_3$ and 138.5$_0$ (*C*H=CH$_2$), 127.7 and 127.3 (IC=*C*H$_2$), 114.1 (CH=*C*H$_2$), 114.1 and 113.2 (MeC=*C*H$_2$), 111.0 and 109.9 (I*C*=CH$_2$), 99.0 and 98.7 (*C*HO$_2$), 81.9 and 81.3 (O*C*Me), 51.2 and 49.8 (O*C*H$_3$), 38.6 and 37.4 (*C*H$_2$CH$_2$CH=), 28.3 and 28.2 (CH$_2$*C*H$_2$CH=), 22.8 and 22.6 (*C*H$_3$) and 18.8 (*C*H$_3$); *m/z* 312.0294 (1%) (*M* − Me, $C_{12}H_{18}O_2I$ requires 321.0352), 267 (2), 252 (4), 251 (45), 225 (14), 198 (16), 197 (100), 182 (89), 167 (28), 153 (10), 128 (10), 127 (20) and 122 (20).

2-(But-3-enyl)-2,3-dimethyl-5-methylidene-6-methoxy-5,6-dihydro-2*H*-pyran 9

A solution of the vinyl iodide **8** (0.120 g, 0.36 mmol), palladium(II) acetate (0.9 mg, 1 mol%), triphenylphosphine (4.2 mg, 4 mol%) and silver(II) carbonate (99 mg, 0.36 mmol) in dry acetonitrile (20 cm^3) was stirred at room temperature for 9 h under an atmosphere of nitrogen. The resulting mixture was filtered through Celite and the solvent removed under reduced pressure to leave a brown residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (pentane) to give the *triene* **9** (47 mg, 62%), predominantly one stereoisomer, as a clear oil; ν_{max}/cm^{-1}(film) 3077, 2973, 1640, 1445, 1396, 1371, 1216, 1188, 1131, 1101, 1049, 965 and 905; δ_H(400 MHz) major isomer: 5.87 (1 H, br s, MeC=C*H*), 5.81–5.71 (1 H, ddt, *J* 17.0, 10.3 and 6.6, C*H*=CH$_2$), 5.05 (1 H, s, C*H*O$_2$), 4.99–4.81 (4 H, m, 2 × CH$_2$), 3.45 (3 H, s, OCH_3), 2.04–1.96 (2 H, m, CH_2), 1.75–1.58 (2 H, m, CH_2), 1.68 (3 H, s, CH_3) and 1.27 (3 H, s, CH_3); δ_C(100 MHz) major isomer: 141.7 (=*C*–), 139.7 (=*C*–), 139.1 (=*C*H), 122.3 (=*C*H), 114.2 (=*C*H$_2$), 109.3 (=CH$_2$), 97.3 (*C*HO$_2$), 78.1 (O*C*Me), 55.5 (O*C*H$_3$), 38.7 (*C*H$_2$CH$_2$CH=), 27.8 (CH$_2$*C*H$_2$CH=), 24.1 (*C*H$_3$) and 19.3 (*C*H$_3$); *m/z* 208.1466 (5%) (*M*, $C_{13}H_{20}O_2$ requires 208.1463), 154 (11), 153 (100), 135 (4), 125 (10), 123 (14), 122 (8), 119 (27) and 107 (14).

5-(But-3-enyl)-4,5-dimethyl-3-methylidene-2-methoxytetrahydrofuran-4-ylmethyl[cobalt(III)salophen]complex 10

A solution of the iodoacetal **8** (0.293 g, 0.87 mmol) in dry deoxygenated THF (5 cm^3) was injected dropwise (syringe) over 1 min to a stirred green solution of sodium cobalt(I) salophen

(0.651 g, 1.74 mmol) in dry deoxygenated THF (120 cm^3) in the dark under an atmosphere of nitrogen. The resulting mixture was stirred for 3 h in the dark under nitrogen and then filtered under reduced pressure in the dark to give a brown crystalline residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel in the dark (methanol–chloroform, 1 : 10) to give the *cobalt salophen complex* **10** (280 mg, 47%), a *ca.* 1 : 1 mixture of diastereoisomers, as an unstable black solid, mp 102–106 °C dec.; ν_{max}/cm^{-1} ($CHCl_3$) 3067, 2922, 1666, 1610, 1579, 1525, 1374, 1338, 1192 and 915; δ_H(400 MHz) 8.50 and 8.44 (2 H, 2 × s, 2 × *H*C=N), 7.68 (2 H, br s, 2 × Ar*H*), 7.48–7.00 (8 H, m, 8 × Ar*H*), 6.60 (2 H, br s, 2 × Ar*H*), 5.78–5.70 (1 H, m, C*H*=CH_2), 4.96–4.85 (3 H, C*H*O_2 + CH=CH_2), 4.35–4.26 (2 H, m, CH=CH_2), 3.71 and 3.48 (2 H, 2 × m, CoCH_2), 3.11 and 3.08 (3 H, 2 × s, OCH_3), 2.04–1.51 (4 H, br m, 2 × CH_2), 1.34–1.32 (3 H, br s, CH_3) and 0.72 and 0.62 (3 H, 2 × s, CH_3); *m/z* (FAB) 582 (6%) (*M*, $C_{33}H_{35}N_2O_4Co$ requires 582.1929), 526 (8), 412 (10), 374 (100), 373 (60), 270 (43), 269 (39) and 211 (67).

Methyl 2-acetyl-2-(2-iodobenzyl)pent-4-enoate 13

A solution of methyl 2-acetylpent-4-enoate [13] (2.34 g, 15 mmol) in THF (2 cm^3) was slowly added to an ice-cooled suspension of sodium hydride (0.618 g, 60% dispersion in oil, 15.4 mmol), previously washed with dry light petroleum (2 × 25 cm^3) in dry THF (40 cm^3), under nitrogen. The mixture was stirred for 10 min under nitrogen and then a solution of 2-iodobenzyl chloride (3.97 g, 15.4 mmol) in THF (3 cm^3) was added over 30 min. The mixture was boiled under reflux under nitrogen for 24 h. Aqueous hydrochloric acid (2 mol dm^{-3}; 10 cm^3) was added to the cooled mixture (0 °C) mixture, followed by saturated aqueous ammonium chloride (10 cm^3). The mixture was then extracted with ether (3 × 25 cm^3). The combined organic phases were washed with saturated aqueous sodium hydrogen carbonate (20 cm^3) and brine (20 cm^3) and then dried ($MgSO_4$). Filtration, followed by removal of the solvent under reduced pressure gave a yellow oil which on chromatography over silica gel (5% ether–dichloromethane) gave the *iodobenzyl β-keto ester* **13** (4 g, 72%) as a pale yellow liquid; ν_{max}/cm^{-1} (film) 3077, 2980, 2950, 2842, 1713, 1640, 1356, 1273, 1212, 1172, 1136, 1050, 1012, 923 and 754; δ_H(270 MHz) 7.85 (1 H, dd, *J* 8 and 2, ArH-3), 7.24 (1 H, t, *J* 8, ArH-5), 7.16 (1 H, dd, *J* 8 and 2, ArH-6), 6.89 (1 H, t, *J* 8, ArH-4), 5.72 (1 H, ddt, *J* 17, 10 and 7, C*H*=CH_2), 5.07–5.13 (2 H, m, CH=CH_2), 3.69 (3 H, s, CO_2Me), 3.52 (1 H, d, *J* 15, ArCH*H*), 3.37 (1 H, d, *J* 15, ArCH*H*), 2.72 (1 H, dd, *J* 15 and 7, CH_2=CH–C*H*H), 2.63 (1 H, dd, *J* 15 and 7, CH_2=CH–CH*H*), 2.13 (3 H, s, CH_3CO); δ_C(68 MHz) 203.9 (Me*C*=O), 171.7 (MeO*C*=O), 139.8 (=*C*H), 139.6 (=*C*–), 132.4 (=*C*H), 130.0 (=*C*H), 128.4 (=*C*H), 128.0 (=*C*H), 119.0 (CH=CH_2), 102.7 (=*C*–), 64.6 [*C*C(O)Me], 52.3 (OCH_3), 41.7 (CH_2), 37.3 (CH_2) and 27.8 ($COCH_3$); *m/z* 245.1143 (34%) (*M* − I, $C_{15}H_{17}O_3$ requires 245.1177), 217 (35), 203 (37), 185 (11), 143 (25) and 127 (9).

3-(2-Iodobenzyl)hex-5-en-2-one 15

A mixture of methyl 2-acetyl-2-(2-iodobenzyl)pent-4-enoate (4 g, 10.75 mmol), lithium chloride (0.912 g, 21.5 mmol), dimethyl sulfoxide (16 cm^3) and water (0.38 g) was stirred at 150 °C for 3 h. The resulting mixture was cooled (ice) and then water (160 cm^3) was added followed by saturated brine (20 cm^3). The mixture was extracted with ether (3 × 30 cm^3), and the ether extract was then washed with saturated brine and dried ($MgSO_4$). Filtration, followed by removal of the solvent under reduced pressure gave the crude product as a yellow oil which upon chromatography over silica gel (light petroleum, stepwise ether gradient to 30%), gave the *iodobenzyl hexenone* **15** (2.6 g, 77%) as a light yellow liquid; ν_{max}/cm^{-1} (film) 3075, 3005, 2926, 1713, 1640, 1585, 1561, 1364, 1011, 918 and 754; δ_H(270 MHz) 7.82 (1 H, dd, *J* 7.9 and 1.3, ArH-3), 7.25 (1 H, t, *J* 7.6, ArH-5), 7.15 (1 H, dd, *J* 7.6 and 1.7, ArH-6), 6.90 (1 H, dt, *J* 7.6 and 1.7, ArH-4), 5.76 (1 H, ddt, *J* 17.0, 9.9 and 6.9, C*H*=CH_2), 5.03–5.11 (2 H, m, CH=CH_2), 3.13–2.97 (2 H, dd + m, *J* 12.9 and 8.3, ArC*H*H + CH_2C*H*CH_2), 2.81–2.74 (1 H, dd, *J* 12.9 and 5.6, ArCH*H*), 2.41 (1 H, quint., *J* 7, $ArCH_2CHCHH$), 2.29–2.20 (1 H, m, $ArCH_2CHCHH$) and 2.02 (3 H, s, CH_3CO); δ_C(68 MHz) 210.7 (*C*=O), 141.7 (=*C*CH_2), 139.5 (=*C*H), 134.7 (=*C*H), 130.6 (=*C*H), 128.1 (=*C*H), 117.2 (CH=*C*H_2), 100.4 (=*C*I), 51.5 (*C*H), 41.5 (*C*H_2), 35.5 (*C*H_2) and 30.7 (*C*H_3); *m/z* 272.9800 (22%) (*M* − C_3H_5 requires 272.9788), 217 (59), 187 (M − I, 60), 145 (49), 128 (15), 115 (15) and 107 (17).

2-Methyl-3-(2-iodobenzyl)hexa-1,5-diene 14

Methyltriphenylphosphonium bromide (3.8 g, 10.6 mmol) was added to a stirred suspension of potassium *tert*-butoxide (1.25 g, 10.6 mmol) in dry ether (30 cm^3), under nitrogen, and the mixture was then heated to reflux. After 20 min a solution of the 3-(2-iodobenzyl)hex-5-en-2-one (2.56 g, 8.15 mmol) in ether (5 cm^3) was added slowly over 30 min *via* syringe. The mixture was boiled under reflux for a further 3 h, after which light petroleum (20 cm^3) was added followed by water (20 cm^3). The mixture was extracted with light petroleum (3 × 15 cm^3), and the organic extract was then washed with water (3 × 15 cm^3), dried ($MgSO_4$) and the solvent removed under reduced pressure to leave the crude product as a yellow liquid. Chromatography of the residue over silica gel (petrol with stepwise ether gradient to 20% ether) gave *2-methyl-3-(2-iodobenzyl)hexa-1,5-diene* **14** (1.90 g, 75%) as a colourless liquid; ν_{max}/cm^{-1} (film) 3072, 2973, 2924, 2855, 1643, 1585, 1562, 1374, 1010, 991, 911, 892 and 747; δ_H(270 MHz) 7.81 (1 H, dd, *J* 7.9 and 1.3, ArH-3), 7.23 (1 H, m, ArH-5), 7.11 (1 H, dd, *J* 7.6 and 1.7, ArH-6), 6.87 (1 H, dt, *J* 7.6 and 1.7, ArH-4), 5.81–5.66 (1 H, ddt, *J* 17.0, 9.9 and 6.9, C*H*=CH_2), 5.05–4.96 (2 H, m, CH=CH_2), 4.74 (1 H, s, C=C*H*H), 4.62 (1 H, s, C=CH*H*), 2.80–2.76 (2 H, dd, *J* 7.4 and 3.1, ArCH_2), 2.55 (1 H, m *ca.* quint., CH_2CHCH_2), 2.19 (2 H, t, *J* 7, CH_2=CHCH_2) and 1.68 (3 H, s, CH_3C=); δ_C(68 MHz) 146.0 (=*C*–), 143.1 (=*C*–), 139.4 (=*C*H), 136.8 (=*C*H), 130.4 (=*C*H), 127.7$_3$ (=*C*H), 127.6$_6$ (=*C*H), 115.7 (=*C*H_2), 112.2 (=*C*H_2), 101.0 (=*C*I), 46.8 (*C*H), 44.3 (*C*H_2), 37.0 (*C*H_2) and 19.3 (*C*H_3); *m/z* 312.0345 (2%) (*M*, $C_{14}H_{17}I$ requires 312.0377), 217 (22), 185 (*M* − I, 22), 144 (*M* − I − C_3H_5, 75), 143 (76), 129 (*M* − I − C_3H_5 − CH_3, 82); (Found: C, 53.9; H, 5.6; I, 41.3. Calc. for $C_{14}H_{17}I$: C, 53.8; H, 5.5; I, 40.7%).

***cis*-1,2,3,3a,8,8a-Hexahydro-3a-methyl-2-methylidenecyclopent[*a*]indene 17 and 1-methylidene-3-(propen-2-yl)-1,2,3,4-tetrahydronaphthalene 16**

A solution of the dienylaryl iodide **14** (0.312 g, 1 mmol), palladium(II) acetate (6.7 mg, 0.03 mmol), triphenylphosphine (0.032 g, 0.12 mmol) and silver(II) carbonate (0.55 g, 2 mmol) in dry acetonitrile (10 cm^3) was heated under reflux with stirring under nitrogen for 6 h. The resulting mixture was filtered through Celite and the solvents were then evaporated under reduced pressure. Chromatography of the residue over silica gel (light petroleum) afforded a colourless oil (0.16 g, 87%) consisting of a mixture of **16** and **17** (ratio ~ 1 : 1) which was resistant to further resolution by conventional chromatography. The tricyclic alkene **17** showed: δ_H(250 MHz) 7.20–7.15 (4 H, m, 4 × Ar*H*), 4.73 (2 H, br s, =CH_2), 3.17 (1 H, dd, *J* 16.1 and 7.7, ArC*H*H), 2.75–2.05 (3 H, m, ArCH*H* + 2 × CH_2) and 1.33 (3 H, s, CH_3); δ_C(100 MHz) 152.4 (*C*=CH_2), 151.3 (=*C*–), 142.0 (=*C*–), 126.7 (=*C*H), 126.5 (=*C*H), 124.9 (=*C*H), 123.0 (=*C*H), 105.3 (=*C*H_2), 55.7 (*C*CH_3), 50.6 (*C*H), 46.8 (*C*H_2), 40.1 (*C*H_2), 37.6 (*C*H_2) and 27.2 (*C*H_3); *m/z* 184.1248 (62%) (*M*, $C_{14}H_{16}$ requires 184.1252), 169 (74), 154 (12.5), 142 (45), 130 (27), 129 (100), 128 (88) and 115 (27), and the bicyclic diene **16** showed: δ_H(400 MHz) 7.66 (1 H, d, *J* 9.1, Ar*H*), 7.20–7.11 (3 H, m, 3 × Ar*H*), 5.52 (1 H, s, C=CH*H*), 4.99 (1 H, s, C=C*H*H), 4.80 (2 H, m, MeC=CH_2), 2.94–2.64 (3 H, m, ArCH_2C*H*), 2.47–2.42 (2 H, m, H_2C=CCH_2) and 1.81 (3 H, d, *J* 0.66, CH_3); δ_C(100 MHz) 148.8 (*C*=CH_2), 143.3 (*C*=CH_2), 137.0 (=*C*–), 134.2 (=*C*–), 129.3 (=*C*H), 127.8 (=*C*H), 126.1 (=*C*H),

124.1 (=*C*H), 109.6 (C=*C*H_2), 108.5 (C=*C*H_2), 42.2 (*C*H), 38.4 (*C*H_2), 36.0 (*C*H_2) and 20.8 (*C*H_3); *m/z* 184.1228 (79%) (*M*, $C_{14}H_{16}$ requires 184.1252), 170 (11), 142 (85), 141 (97), 129 (89), 128 (78), 127 (21), 115 (61), 111 (23), 109 (17), 97 (37) and 91 (27).

3-Methyl-2-(prop-2-enyl)-1,2-dihydronaphthalene 18, 2-methyl-3-(prop-2-enyl)-1,4-dihydronaphthalene 19 and 3-benzyl-2-methylhexa-1,5-diene 20

A solution of the dienylaryl iodide **14** (0.312 g) in dry deoxygenated THF (5 cm^3) was added dropwise over 10 min to a stirred green solution of sodium salophencobaltate(I) (1.12 g, 3 mmol) in THF, under an atmosphere of nitrogen in the dark, and the mixture was then stirred under nitrogen in the dark for 20 h. The solvent was removed by evaporation under reduced pressure, and the residue was then adsorbed onto silica gel. Chromatography over silica gel (dichloromethane) gave a colourless oil (0.12 g) consisting of a mixture (^1H NMR assay) of the dihydronaphthalenes **18** (33%) and **19** (8%), and the reduction product **20** (12%). The mixture was separated by reverse phase HPLC (methanol) to give: (a) 3-*methyl*-2-(*prop*-2-*enyl*)-1,2-*dihydronaphthalene* **18**: δ_H(270 MHz) 7.39–7.22 (3 H, m, 3 × ArH), 7.12 (1 H, d, *J* 6.6, 5-H), 6.37 (1 H, d, *J* 1.3, 4-H), 6.01–5.85 (1 H, *ca.* ddt, *J* 16.8, 10.2 and 5.9, C*H*=CH_2), 5.21–5.16 (2 H, m, CH=CH_2), 3.13–3.05 (1 H, dd, *J* 15.7 and 6.4, ArC*H*H), 2.94–2.87 (1 H, dd, *J* 15.7 and 3.1, ArCH*H*), 2.39–2.00 (3 H, m, C*H*CH_2) and 2.10 (3 H, d, *J* 1.7, CH_3); δ_C(100 MHz) 141.4 (=CMe), 137.2 (*C*H=CH_2), 134.7 (aryl =*C*–), 132.8 (aryl =*C*–), 128.1 (=*C*H), 126.4 (=*C*H), 126.3 (=*C*H), 125.1 (=*C*H), 122.9 (=CH), 116.5 (=CH_2), 38.4 (*C*H), 35.1 (*C*H_2), 32.2 (*C*H_2) and 22.3 (*C*H_3); *m/z* 184.1227 (10%) (*M*, $C_{14}H_{16}$ requires 184.1252), 143 (*M* − C_3H_5, 100), 141 (13), 128 (42) and 115 (10); (b) 2-*methyl*-3-(*prop*-2-*enyl*)-1,4-*dihydronaphthalene* **19**: δ_H(270 MHz) 7.09–7.05 (4 H, m, 4 × Ar*H*), 5.80–5.65 (1 H, ddt, *J* 16.9, 10.2 and 6.5, C*H*=CH_2), 5.02–4.91 (2 H, m, CH=CH_2), 3.26 (2 H, br s, 2 × ArCH_2), 2.84 (2 H, d, *J* 6.3, CH_2CH=) and 1.72 (3 H, s, CH_3); δ_C(100 MHz) 135.9 (*C*H=CH_2), 135.2 (=*C*–), 134.9 (=*C*–), 127.8 (=*C*H), 127.6 (=*C*H), 125.7 (2 × =*C*H), 125.6 (=*C*–), 125.5 (=*C*–), 115.1 (=CH_2), 37.4 (*C*H_2), 36.9 (*C*H_2), 34.6 (*C*H_2) and 18.6 (*C*H_3); *m/z* 184.1217 (5%) (*M*, $C_{14}H_{16}$ requires 184.1252), 182 (65), 167 (82), 165 (34), 143 (*M* − C_3H_5, 23) and 128 (28); and (c) 3-*benzyl*-2-*methylhexa*-1,5-*diene* **20**: δ_H(270 MHz) 7.21–7.05 (5 H, m, 5 × Ar*H*), 5.72–5.56 (1 H, ddt, *J* 17.2, 10.2 and 6.9, C*H*=CH_2), 4.95–4.88 (2 H, m *ca.* 2 × d, CH=CH_2), 4.65 (1 H, d, *J* 1.3, MeC=C*H*H), 4.53 (1 H, s, MeC=CH*H*), 2.60 (2 H, d, *J* 7.3, ArCH_2), 2.35, (1 H, m, *ca.* quint., ArCH_2C*H*), 2.10–2.04 (2 H, m *ca.* dd, CH_2CH=) and 1.59 (3 H, s, Me); δ_C(100 MHz) 146.7 (=*C*Me), 140.9 (aryl =*C*–), 137.2 (*C*H=CH_2), 129.1 (2 × =*C*H), 128.2 (2 × =*C*H), 125.9 (=*C*H), 115.7 (CH=*C*H_2), 111.9 (MeC=*C*H_2), 48.8 (*C*H), 39.9 (*C*H_2), 37.3 (*C*H_2) and 19.4 (*C*H_3); *m/z* 186.1385 (1%) (*M*, $C_{14}H_{18}$ requires 186.1409), 171 (*M* − Me, 3), 145 (*M* − C_3H_5, 36), 130 (11), 129 (15), 117 (18), 95 (75) and 91 (C_3H_7, 100).

***cis*-1,2,3,3a,8,8a-Hexahydro-3a-methylcyclopent[*a*]inden-2-one 22 and 3-acetyl-1,2,3,4-tetrahydronaphthalen-2-one (3-acetyl-1-tetralone) 21**

The mixture of alkenes **16** and **17** was dissolved in dioxane (5.25 cm^3) and water (1.75 cm^3), and a 1% w/v aqueous solution of osmium tetroxide (0.21 cm^3) was then added dropwise. After a few min the solution turned black and potassium periodate (1.05 g) was then added in small portions over 30 min. The solution was left to stir at room temperature for 30 h, then extracted with ether (3 × 20 cm^3). The combined ether extracts were dried ($MgSO_4$), filtered and the solvent was then removed under reduced pressure. The residual colourless oil was purified by chromatography over silica gel (light petroleum–ether, 4:1) to give (i) the tricyclic ketone **22** (40 mg) as a colourless oil: ν_{max}/cm^{-1} (film) 3066, 3017, 2952, 1741, 1477, 1399 and 1166; δ_H(400 MHz) 7.23–7.15 (4 H, m, 4 × Ar*H*), 3.33–3.27 (1 H, dd, *J* 16.6 and 7.7, 8-Hβ), 2.77–2.60 (4 H, m, 8-Hα + 8a-H + 1-Hβ + 3-Hβ), 2.47–2.35 (1 H, m, 3-Hα), 2.10–2.04 (1 H, ddd, *J* 18.8, 6.7 and 1.5, 1-Hα) and 1.40 (3 H, s, CH_3); δ_C(100 MHz) 218.5 (C-2), 149.3 (C-3b), 141.2 (C-7a), 127.3 (=*C*H), 127.2 (=*C*H), 125.5 (=*C*H), 123.3 (=*C*H), 52.5 (C-3a), 50.9 (C-3), 47.1 (C-8a), 44.8 (C-1), 37.2 (C-8) and 27.0 (*C*H_3); *m/z* 186.0970 (48%) (*M*, $C_{13}H_{14}O$ requires 186.1045), 144 (26), 143 (74), 129 (100), 128 (80), 115 (28), and (ii) the 1,4-dione **21** (34 mg), as an oil; ν_{max}/cm^{-1} (film) 3078, 2926, 2853, 1712, 1691, 1605, 1456, 1355, 1300 and 1116; δ_H(400 MHz) 8.02 (1 H, dd, *J* 7.9 and 1.2, 8-H), 7.51 (1 H, dt, *J* 7.5 and 1.3, 6-H), 7.33 (1 H, t, *J* 7.5, 7-H), 7.28 (1 H, dd, *J* 7.8 and 1.3, 5-H), 3.28–3.20 (1 H, m, 3-H), 3.17–3.09 (2 H, m, 4-H_2), 2.92–2.87 (1 H, ddd, *J* 16.9, 3.9 and 1.5, 2-Ha), 2.77–2.70 (1 H, dd, *J* 16.9 and 11.3, 2-Hb) and 2.26 (3 H, s, CH_3); δ_C(100 MHz) 207.9 (*C*OMe), 196.2 (C-1), 141.5 (C-8a), 134.0 (C-6), 132.0 (C-4a), 128.9 (C-5), 127.3 (C-7 + C-8), 48.1 (C-3), 40.4 (C-2), 31.5 (C-4) and 28.1 (Me); *m/z* 188.0831 (3%) (*M*, $C_{12}H_{12}O_2$ requires 188.0837), 170 (10), 146 (49), 145 (100), 131 (24), 127 (17), 117 (55), 115 (54) and 91 (25).

Conversion of the ketones 21 and 22 into the olefins 16 and 17 respectively by Wittig olefination reactions

Potassium *tert*-butoxide (39 mg, 0.351 mmol) was stirred in dry ether (2 cm^3) under an atmosphere of nitrogen, and methyltriphenylphosphonium bromide (125 mg, 0.351 mol) was added. The mixture was boiled under reflux under nitrogen for 20 min, and then a solution of the ketone **21** (or **22**) (30 mg, 0.159 mmol) in dry ether (1 cm^3) was added dropwise (syringe). The mixture was heated for a further 3 h, and then the mixture was cooled to room temperature, quenched with water (10 cm^3), and extracted with light petroleum (3 × 10 cm^3). The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was then removed under reduced pressure to leave a semi-solid residue. The residue was washed with pentane (3 × 5 cm^3) and the pentane extracts were evaporated to leave a residue which was purified by chromatography over silica gel (light petroleum) to give the *olefin* **16** (or **17**) (10–12 mg). The spectroscopic data recorded for the reconstituted alkenes were identical to those listed earlier.

Diethyl (2-iodobenzyl)(prop-2-enyl)malonate 23

A solution of diethyl allylmalonate (7 g, 0.035 mol) in THF (5 cm^3) was added over 10 min to an ice-cooled suspension of sodium hydride (1.46 g, 60% dispersion in oil, 0.036 mol), previously washed with dry light petroleum (2 × 25 cm^3) in dry THF (50 cm^3) under nitrogen. The mixture was stirred for 20 min under nitrogen and then a solution of 2-iodobenzyl chloride (9.27 g, 0.036 mol) in THF (5 cm^3) was added dropwise over 15 min. The mixture was boiled under reflux under an atmosphere of nitrogen for *ca.* 24 h, and then cooled in ice. Aqueous hydrochloric acid (2 mol dm^{-3}; 20 cm^3) was added, followed by saturated aqueous ammonium chloride (20 cm^3). The mixture was extracted with ether (3 × 30 cm^3) and the combined ether extracts were then washed with saturated aqueous sodium hydrogen carbonate (2 × 20 cm^3), brine (2 × 20 cm^3), and dried ($MgSO_4$). Filtration followed by removal of the solvent under reduced pressure left the crude product as an oil which was purified by chromatography over silica gel (light petroleum with stepwise CH_2Cl_2 gradient to 60%) to give the *benzylmalonate* **23** (12.2 g, 84%); ν_{max}/cm^{-1} (film) 3078, 2981, 2937, 2906, 1729, 1641, 1587, 1562, 1282, 1217, 1141, 1041, 1012, 922 and 749; δ_H(270 MHz) 7.83 (1 H, d, *J* 7.9, ArH-3), 7.27–7.21 (2 H, m, 2 × Ar*H*), 6.92–6.86 (1 H, m, Ar*H*), 5.92–5.77 (1 H, ddt, *J* 17.2, 9.9 and 7.3, C*H*=CH_2), 5.14–5.07 (2 H, m, CH=CH_2), 4.21–4.07 (4 H, m, 2 × OCH_2CH_3), 3.50 (2 H, s, ArCH_2), 2.68 (2 H, d, *J* 7.3, CH_2CH=CH_2) and 1.19 (6 H, t, *J* 6.9, 2 × OCH_2CH_3); δ_C(68 MHz) 170.2 (2 × *C*=O), 139.6 (=*C*–), 132.7 (=*C*H), 132.0 (=*C*H), 129.8 (=*C*H), 128.1 (=*C*H), 127.7 (=*C*H), 118.7 (=CH_2), 102.6 (=*C*I), 61.0 (2 × O*C*H_2), 60.8 and 58.5 [*C*(CO_2Et)$_2$], 42.2 (*C*H_2), 36.4 (*C*H_2) and 13.6 (2 × OCH_2*C*H_3); *m/z* 199.0975

(21%) (M − C_7H_6I requires 199.0970), 324 (3), 298 (3), 153 (100), 149 (21), 148 (10) and 125 (37).

Ethyl 2-(2-iodobenzyl)pent-4-enoate 24

A mixture of diethyl (2-iodobenzyl)(prop-2-enyl)malonate (8.15 g, 19.5 mmol), lithium chloride (1.66 g, 39 mmol), water (0.7 g) and dimethyl sulfoxide (32 cm^3) was stirred at 170 °C for 8 h. The mixture was cooled in ice, and then water (320 cm^3) was added followed by brine (20 cm^3). The mixture was extracted with ether (3 × 30 cm^3), and the combined ether extracts were then washed with saturated brine and dried ($MgSO_4$). Filtration followed by removal of the solvent under reduced pressure left an oil which was purified by chromatography over silica gel (light petroleum with stepwise CH_2Cl_2 gradient to 30%) to give the *γ,δ-unsaturated ester* **24** (5.77 g, 83%); ν_{max}/cm^{-1} (film) 3078, 2980, 2936, 1733, 1642, 1586, 1563, 1376, 1186, 1162, 1013, 918 and 750; δ_H(270 MHz) 7.73 (1 H, dd, *J* 7.9 and 1.0, ArH-3), 7.18–7.09 (2 H, m, ArH-4,6), 6.84–6.78 (1 H, m *ca.* ddd, ArH-5), 5.81–5.65 (1 H, ddt, *J* 17.2, 10.2 and 6.9, C*H*=CH_2), 5.06–4.96 (2 H, m, CH=CH_2), 4.01–3.92 (2 H, dq, *J* 7.2 and 1.7, OCH_2), 3.01–2.91 (1 H, dd, *J* 14.8 and 10.9, ArC*H*H), 2.86–2.75 (2 H, m + dd, *J* 14.8 and 5.3, ArCH*H* and ArCH_2C*H*), 2.42–2.20 (2 H, m, CH_2CH=CH_2) and 1.05 (3 H, t, *J* 7.1, CH_3); δ_C(68 MHz) 174.3 (*C*=O), 141.8 (=C–), 139.5 (=CH), 134.8 (=CH), 130.3 (=CH), 128.1 (=CH), 128.0 (=CH), 117.2 (CH=CH_2), 100.6 (=*C*I), 60.1 (OCH_2), 45.2 (*C*H), 42.2 (CH_2), 36.4 (CH_2) and 14.1 (CH_3); *m/z* 302.9835 (11%) (M − C_3H_5 requires 302.9882), 217 (M − I, 100), 189 (43), 147 (27), 128 (18), 127 (23) and 115 (15).

2-(2-Iodobenzyl)pent-4-enal 26

A 1.5 mol dm^{-3} solution of diisobutylaluminium hydride in toluene (11.74 cm^3 17.6 mmol) was added dropwise over 20 min to a stirred solution of ethyl (2-iodobenzyl)(prop-2-enyl)-malonate (5.77 g, 16.8 mmol) in dry toluene (50 cm^3) at −78 °C under an atmosphere of nitrogen. The mixture was stirred at −78 °C for a further 2 h, and then allowed to warm to 0 °C. Acetone (4 cm^3) was added followed by water (8 cm^3) and then aqueous hydrochloric acid (2 mol dm^{-3}; 20 cm^3). The mixture was extracted with ether (3 × 30 cm^3), and the combined ether extracts were then washed with brine and dried ($MgSO_4$). Filtration followed by removal of the solvent under reduced pressure left an oil, which was purified by chromatography over silica gel (light petroleum–ether, 9:1) to give the *pentenal* **26** (4.02 g, 80%); ν_{max}/cm^{-1} (film) 3078, 3007, 2980, 2927, 2857, 2726, 1728, 1641, 1586, 1563, 1217, 1189, 1162, 1012, 919 and 754; δ_H(400 MHz) 9.72 (1 H, d, *J* 1.8, C*H*O), 7.83 (1 H, d, *J* 7.9, aryl 3-H), 7.28–7.19 (2 H, m, aryl 5-H and aryl 6-H), 6.93–6.89 (1 H, m *ca.* dt, aryl 4-H), 5.84–5.74 (1 H, ddt, *J* 17.0, 10.2 and 7.0, C*H*=CH_2), 5.14–5.09 (2 H, m, CH=CH_2), 3.16–3.10 (1 H, dd, *J* 13.5 and 7.3, ArC*H*H), 2.92–2.85 (1 H, m *ca.* quint., CH_2CHCH_2), 2.84–2.79 (1 H, dd, *J* 13.5 and 6.7, ArCH*H*) and 2.48–2.32 (2 H, m, CH_2=CHCH_2); δ_C(100 MHz) 203.4 (*C*HO), 141.6 (=*C*–), 139.9 (=*C*H), 134.4 (=*C*H), 130.8 (=*C*H), 128.4$_5$ (=*C*H), 128.3$_8$ (=*C*H), 118.0 (CH=*C*H_2), 100.8 (=*C*I), 51.2 (*C*H), 39.2 (CH_2) and 33.1 (CH_2); *m/z* 298.9951 (2%) (M − H, $C_{12}H_{12}IO$ requires 298.9933), 259 (19), 217 (100), 173 (M − I, 28), 131 (34), 127 (2.5), 115 (13), 107 (27) and 91 (47).

3-(2-Iodobenzyl)hexa-1,5-diene 25

Methyltriphenylphosphonium bromide (5.34 g, 14.6 mmol) was added to a stirred suspension of potassium *tert*-butoxide (1.73 g, 14.6 mmol) in dry ether (30 cm^3) under an atmosphere of nitrogen, and the mixture was then heated under reflux for 20 min. A solution of 2-(2-iodobenzyl)pent-4-enal (4 g, 13.3 mmol) in ether (3 cm^3) was added over 10 min, and the mixture was then boiled under reflux for a further 1.5 h. Light petroleum (30 cm^3) was added followed by water (20 cm^3), and the mixture was then extracted with light petroleum (3 × 15 cm^3). The combined organic extracts were washed with water (3 × 15 cm^3), dried ($MgSO_4$), and the solvent was then removed under reduced pressure. Chromatography of the residue over silica gel (light petroleum with stepwise ether gradient to 10% ether) gave 3-(2-*iodobenzyl*)*hexa*-1,5-*diene* **25** (2.64 g, 66%) as a colourless liquid; ν_{max}/cm^{-1} (film) 3076, 2978, 2922, 1641, 1467, 1012, 915 and 749; δ_H(400 MHz) 7.82–7.80 (1 H, dd, *J* 7.9 and 1.1, aryl 3-H), 7.25–7.21 (1 H, td, *J* 7.4 and 1.0, aryl 5-H), 7.13–7.10 (1 H, dd, *J* 7.6 and 1.7, aryl 6-H), 6.89–6.84 (1 H, td, *J* 7.6 and 1.6, aryl 4-H), 5.86–5.76 (1 H, ddt, *J* 17.1, 10.2 and 7.0, C*H*=CH_2), 5.73–5.64 (1 H, ddd, *J* 17.1, 10.3 and 8.3, C*H*=CH_2), 5.07–5.01 (2 H, m, CH=CH_2), 4.96–4.93 (1 H, dd, *J* 10.3 and 1.7, CH=C*H*H), 4.88–4.83 (1 H, dd, *J* 15.6 and 1.0, CH=CH*H*), 2.86–2.81 (1 H, dd, *J* 13.6 and 6.3, ArC*H*H), 2.70–2.65 (1 H, dd, *J* 13.6 and 8.3, ArCH*H*), 2.56–2.47 (1 H, m *ca.* quint., CH_2CHCH_2) and 2.27–2.14 (2 H, m, CH_2=CHCH_2); δ_C(68 MHz) 143.1 (=*C*–), 141.0 (=*C*H), 139.6 (=*C*H), 136.7 (=*C*H), 130.9 (=*C*H), 127.9 (2 × *C*H), 116.5 (=CH_2), 115.4 (=CH_2), 101.4 (=*C*I), 45.5 (CH_2), 43.9 (*C*H) and 38.9 (CH_2); *m/z* 298.0211 (5%) (M, $C_{13}H_{15}I$ requires 298.0219), 244 (2), 217 (M − C_6H_9, 100), 171 (M − I, 28), 130 (M − I − C_3H_5, 91) and 127 (12) (Found: C, 52.4; H, 5.3; I, 43.0. Calc. for $C_{13}H_{15}I$: C, 52.4; H, 5.1; I, 42.6%).

1-Methylidene-2-(prop-2-enyl)indane 27

A stirred solution of the dienylaryl iodide **25** (0.298 g, 1 mmol), palladium(II) acetate (6.7 mg, 0.03 mmol), triphenylphosphine (0.032 g, 0.12 mmol) and silver(II) carbonate (0.55 g, 2 mmol) in dry acetonitrile (10 cm^3), was boiled under reflux under nitrogen for 24 h. The mixture was cooled to room temperature, and then filtered through Celite. The solvent was evaporated under reduced pressure to leave an oil which was purified by chromatography over silica gel (light petroleum) to give the *methylidene indane* **27** (0.114 g, 67%) as a colourless oil; ν_{max}/cm^{-1} (film) 3072, 3023, 2927, 1714, 1640, 1604, 1474, 1460, 993 and 914; δ_H(270 MHz) 7.37–7.05 (4 H, m, 4 × ArH), 5.80–5.65 (1 H, ddt, *J*17.0, 10.1 and 6.9, C*H*=CH_2), 5.40 (1 H, d, *J* 2.0, ArC=C*H*H), 4.99–4.90 (3 H, m, ArC=CH*H* + CH=CH_2), 2.99–2.93 (2 H, m, ArCH_2), 2.81–2.56 (1 H, m), 2.38–2.24 (1 H, m) and 2.15–2.07 (1 H, m); δ_C(68 MHz) 153.8 (=*C*–), 144.9 (=C–), 140.8 (=C–), 136.6 (*C*H=CH_2), 128.4 (=*C*H), 126.5 (=*C*H), 125.2 (=*C*H), 120.7 (=*C*H), 116.1 (=CH_2), 102.8 (=CH_2), 42.3 (*C*H), 39.8 (CH_2) and 36.3 (CH_2); *m/z* 170.0961 (98%) (M, $C_{13}H_{14}$ requires 170.1096), 168 (17), 157 (17), 155 (44), 145 (22), 143 (21), 141 (33), 132 (27), 130 (33), 129 (85) and 128 (38).

2-(Prop-2-enyl)indan-1-ylmethylcobalt(III) salophen 28

A solution of iodobenzylhexa-1,5-diene **25** (0.3 g, 1 mmol) in dry deoxygenated THF (5 cm^3) was added dropwise over 10 min to a stirred green solution of sodium salophencobaltate(I) (1.12 g, 3 mmol) in THF, under an atmosphere of nitrogen in the dark. The mixture was stirred in the dark for 2 h and then the solvent was removed by evaporation under reduced pressure. The residue adsorbed onto silica gel, and purified by chromatography in the dark over silica gel (CH_2Cl_2–MeOH, 20:1) to afford unchanged starting material (0.086 g, 29%), and the cobalt(III) salophen **28** (0.359 g, 66%) as a black solid, mp (dec.) > 144 °C; ν_{max}/cm^{-1} ($CHCl_3$) 2992, 2914, 2845, 1944, 1714, 1611, 1576, 1526, 1492, 1460, 1440, 1372, 1338, 1150, 1132, 951, 913 and 864; δ_H(400 MHz) 8.68 (1 H, s, ArC*H*=N), 8.63 (1 H, s, ArC*H*=N), 7.90–7.84 (2 H × Ar*H* salophen), 7.50–7.23 (8 H, m, 8 × Ar*H* salophen), 7.22–6.92 (4 H, m, 4 × Ar*H*), 6.71 (1 H, d, *J* 8.2, Ar*H* salophen), 6.67 (1 H, d, *J* 8.2, Ar*H* salophen), 5.48–5.38 (1 H, m, C*H*=CH_2) 4.80 (1 H, d, *J* 10.2, CH=C*H*H), 4.73 (1 H, d, *J* 17.1, CH=CH*H*), 3.01–2.99 (1 H, dd, *J* 6.4 and 3.8, C*H*H–Co), 2.90–2.86 (1 H, dd, *J* 8.3 and 6.4, CH*H*–Co), 2.70–2.64 (1 H, dd, *J* 16.1 and 7.4, ArC*H*H), 2.33–2.28 (1 H, dd, *J* 16.1 and 3.2, ArCH*H*), 2.15–2.04 (1 H, m, ArCH_2C*H*), 1.86–1.75 (1 H, m, ArC*H*CH_2Co) and 1.64–1.47 (2 H, m, CH_2CH=); δ_C(68 MHz) 168.1 (=*C*–), 167.9 (=*C*–), 155.5 (=*C*H), 155.3 (=*C*H), 144.3 (2 × =*C*–), 144.2 (=*C*–), 141.7 (=*C*–),

137.8 (=*C*H), 134.3 (2 × =*C*H), 133.8 (=*C*H), 133.7 (=*C*H), 126.7 (2 × =*C*H), 126.2 (=*C*H), 125.9 (=*C*H), 124.8 (=*C*H), 124.6 (=*C*H), 124.2 (=*C*H), 124.1 (=*C*H), 119.6$_2$ (=*C*–), 119.5$_7$ (=*C*–), 116.1 (2 × =*C*H), 115.1 (=*C*H$_2$), 114.4 (=*C*H), 114.2 (=*C*H), 55.0 (*C*H), 43.1 (*C*H), 38.8 (*C*H$_2$), 35.0 (*C*H$_2$) and 23.1 (*C*H$_2$); *m/z* (FAB) 545 (8%) (*M* + H, $C_{33}H_{29}N_2O_2Co$ requires 544), 390 (6), 374 (100), 307 (7), 280 (7), 171 (8), 154 (51), 136 (41), 107 (20), 91 (23), 77 (21) and 69 (37).

2-(Prop-2-enyl)-3-methylindene 30 and 4,4a,9,9a-tetrahydro-1*H*-fluorene 29

A solution of the salophen complex **28** (0.26 g, 0.47 mmol) in dry benzene (120 cm^3) was deoxygenated and then photolysed under a nitrogen atmosphere for 20 h. The solvent was evaporated under reduced pressure and the residue was then purified by chromatography over silica gel (light petroleum) to give a colourless oil (40 mg, 50%) consisting of a 2:1 mixture of **29** and **30**. The mixture was separated by reverse phase HPLC (methanol) to give: (*i*) the diene **30** as an oil; δ_H(270 MHz) 7.38 (1 H, d, *J* 7.3, Ar*H*), 7.28–7.10 (3 H, m, 3 × Ar*H*), 5.96–5.81 (1 H, ddt, *J* 16.7, 10.0 and 6.5, C*H*=CH$_2$), 5.10–5.01 (2 H, m, CH=C*H*$_2$), 3.29 (2 H, s, ArC*H*$_2$), 3.22 (2 H, d, *J* 6.3, C*H*$_2$CH=CH$_2$) and 2.06 (3 H, s, C*H*$_3$); δ_C(100 MHz) 147.3 (*C*=CH$_2$), 142.6 (=*C*–), 139.7 (=*C*–), 136.4 (=*C*H), 133.4 (=*C*–), 126.1 (=CH), 123.9 (=*C*H), 123.2 (=*C*H), 118.3 (=*C*H), 115.3 (=*C*H$_2$), 40.4 (*C*H$_2$), 33.0 (*C*H$_2$) and 10.2 (*C*H$_3$); *m/z* 170.1105 (55%) (*M*, $C_{13}H_{14}$ requires 170.1096), 155 (*M* − Me, 34), 129 (100), 115 (15) and 91 (4.5), and (*ii*) the cyclohexene **29**, as a colourless liquid: δ_H(400 MHz) 7.26–7.24 (1 H, m, Ar*H*), 7.20–7.13 (3 H, m, 3 × Ar*H*), 5.82–5.81 (2 H, m, C*H*=C*H*), 2.99–2.94 (1 H, dd, *J* 14.6 and 6.7, ArC*H*H), 2.75–2.68 (2 H, m, ArC*H*C*H*H), 2.57–2.51 (1 H, dd, *J* 14.6 and 11.6, ArCH*H*), 2.38–2.33 (1 H, m, ArCH$_2$CHCH*H*), 2.21–2.10 (2 H, m, CH*H*CH=CHCH*H*) and 2.00–1.94 (1 H, m, ArCH$_2$C*H*); δ_C(100 MHz) 146.8 (=*C*–), 144.1 (=*C*–), 128.2 (=*C*H), 126.8 (=*C*H), 126.2 (=*C*H), 126.1 (=*C*H), 124.5 (=*C*H), 122.3 (=*C*H), 46.4 (*C*H), 45.4 (*C*H), 37.9 (*C*H$_2$), 31.3 (*C*H$_2$) and 29.7 (*C*H$_2$); *m/z* 170.1044 (7%) (*M*, $C_{13}H_{14}$ requires 170.1096), 163 (18), 151 (5), 113 (24), 97 (27), 85 (39), 71 (48), 57 (72) and 40 (100).

Methyl 2-(2-iodobenzyl)-3-oxohept-6-enoate 31

A solution of methyl 3-oxohept-6-enoate[14] (0.500 g, 3.21 mmol) in dry diethyl ether (5 cm^3) was added dropwise over 5 min to a stirred suspension of sodium hydride (60% dispersion, 0.141 g, 3.53 mmol) in dry diethyl ether (40 cm^3) under an atmosphere of nitrogen. The resulting mixture was stirred for 20 min under nitrogen, after which a solution of 2-iodobenzyl chloride (0.892 g, 3.53 mmol) in dry diethyl ether (5 cm^3) was added dropwise over 5 min. The reaction mixture was heated under reflux for 36 h under an atmosphere of nitrogen, and then cooled to 0 °C. Water (15 cm^3) was added to the resulting suspension and the solution was then washed with diethyl ether (3 × 50 cm^3). The combined organic phases were washed with brine (20 cm^3), dried ($MgSO_4$), filtered and the solvent removed at reduced pressure to leave a yellow liquid. The liquid was purified by chromatography over silica gel (diethyl ether–light petroleum, 1:10) to give the *iodobenzyl β-keto ester* **31** (0.298 g, 43% based on recovered starting material) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3065, 2953, 1745, 1716, 1641, 1588, 1565, 1466, 1436, 1263, 1208, 1015 and 917; δ_H(270 MHz) 7.84 (1 H, d, *J* 7.9, Ar*H*), 7.29–7.11 (2 H, m, 2 × Ar*H*), 6.91 (1 H, m, Ar*H*), 5.85 (1 H, ddt, *J* 17.2, 10.6 and 6.6, C*H*=CH$_2$), 5.09 (1 H, dd, *J* 17.2 and 1.7, CH=C*H*$_2$), 5.04 (1 H, dd, *J* 10.6 and 1.7, CH=C*H*$_2$), 4.18 (1 H, m, C*H*CO$_2$Me), 3.71 (3 H, s, OC*H*$_3$), 3.23 (2 H, d, *J* 7.6, ArC*H*$_2$), 2.69 (2 H, t, *J* 7.3, C*H*$_2$CO) and 2.35 (2 H, dt, *J* 7.6 and 6.6, C*H*$_2$CH=CH$_2$); δ_C(68 MHz) 203.5 (*C*O), 169.0 (*C*O$_2$), 140.4 (=*C*–), 139.8 (=CH), 136.5 (=*C*H), 134.2 (=*C*H), 131.0 (=*C*H), 128.8 (=*C*H), 115.4 (=*C*H$_2$), 99.5 (=*C*I), 58.0 (*C*H), 52.4 (O*C*H$_3$), 42.0 (*C*H$_2$), 32.2 (*C*H$_2$) and 22.4 (*C*H$_2$); *m/z* 288.9723 (42%) (*M* − C_5H_7O, $C_{10}H_{10}O_2I$ requires 288.9726), 245 (45), 217 (*M* − $C_8H_{11}O_3$, 31), 185 (23), 127 (3), 121 (10) and 83 (57).

1-(2-Iodophenyl)hept-6-en-3-one 32

A solution of methyl 2-(2-iodobenzyl)-3-oxohept-6-enoate (0.198 g, 0.53 mmol) in aqueous sodium hydroxide (5 mol dm^{-3}; 10 cm^3) was heated under reflux for 10 h. The resulting suspension was dissolved in water (15 cm^3) and extracted into diethyl ether (3 × 25 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed at reduced pressure to leave a yellow liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:5) to give *iodophenylheptenone* **32** (0.112 g, 67%) as a colourless oil; ν_{max}/cm^{-1} (film) 2923, 1714, 1641, 1466, 1435, 1366, 1010 and 913; δ_H(270 MHz) 7.81 (1 H, dd, *J* 7.3 and 1.0, ArH-3), 7.29–7.16 (2 H, m, ArH-4,6), 6.92–6.86 (1 H, m, *ca.* ddd, ArH-5), 5.88–5.73 (1 H, ddt, *J* 17.2, 10.2 and 6.6, C*H*=CH$_2$), 5.07–4.90 (2 H, m, CH=C*H*$_2$), 3.00 (2 H, *ca.* t, *J* 7.7, ArC*H*$_2$), 2.73 (2 H, *ca.* t, *J* 7.7, ArCH$_2$C*H*$_2$CO), 2.53 (2 H, t, *J* 7.4, =CHCH$_2$C*H*$_2$CO) and 2.41–2.30 (2 H, m, C*H*$_2$CH=CH$_2$); δ_C(68 MHz) 208.9 (*C*=O), 143.5 (=*C*–), 139.5 (=*C*H), 137.0 (*C*H=CH$_2$), 129.7 (=*C*H), 128.5 (*C*H), 128.1 (=*C*H), 115.3 (=*C*H$_2$), 100.2 (=*C*I), 42.8 (*C*H$_2$), 41.9 (*C*H$_2$), 34.8 (*C*H$_2$) and 27.8 (*C*H$_2$); *m/z* 258.9603 (7%) (*M* − C_4H_7 requires 258.9620), 216.9532 (59) (*M* − C_6H_9O requires 216.9514), 187.1107 (100) (*M* − I requires 187.1123), 145 (27), 104 (44) and 55 (71).

7-(2-Iodophenyl)-5-methylidenehept-1-ene 33

A stirred suspension of potassium *tert*-butoxide (0.322 g, 2.87 mmol) and methyltriphenylphosphonium bromide (1.03 g, 2.87 mmol) in dry diethyl ether (30 cm^3) was stirred under reflux for 20 min under an atmosphere of nitrogen. The resulting yellow solution was allowed to cool to *ca.* 30 °C, and a solution of 1-(2-iodophenyl)hept-6-en-3-one (0.695 g, 2.21 mmol) in dry diethyl ether (5 cm^3) was then added dropwise over 5 min under an atmosphere of nitrogen. Water (10 cm^3) was added and then the solution was extracted with diethyl ether (3 × 30 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed at reduced pressure to leave a yellow liquid. The liquid was purified by chromatography over silica gel (diethyl ether–light petroleum) to give the *alkene* **33** (0.530 g, 73%) as a colourless oil; ν_{max}/cm^{-1} (film) 3075, 2927, 2854, 1642, 1604, 1586, 1562, 1466, 1435, 1012, 911, 891 and 748; δ_H(270 MHz) 7.69 (1 H, d, *J* 7.9, ArH-3), 7.15–7.07 (2 H, m, ArH-4,6), 6.79–6.72 (1 H, m *ca.* ddd, ArH-5), 5.80–5.66 (1 H, ddt, *J* 17.2, 10.0 and 6.3, C*H*=CH$_2$), 4.97–4.90 (1 H, dd, *J* 17.2 and 1.7, CH=CH*H*), 4.87 (1 H, d, *J* 10.0, CH=C*H*H), 4.72 and 4.70 (2 H, 2 × s, C=C*H*$_2$), 2.76–2.70 (2 H, m *ca.* dd, ArC*H*$_2$) and 2.20–2.05 (6 H, m, 3 × C*H*$_2$); δ_C(68 MHz) 148.6 (=*C*–), 145.0 (=*C*–), 139.9 (=*C*H), 138.8 (=*C*H), 129.7 (=*C*H), 128.8 (=*C*H), 128.1 (=*C*H), 115.1 (CH=*C*H$_2$), 110.3 (C=*C*H$_2$), 100.9 (=*C*I), 40.0 (*C*H$_2$), 37.0 (*C*H$_2$), 35.9 (*C*H$_2$) and 32.5 (*C*H$_2$); *m/z* 216.9523 (100%) (*M* − C_7H_{11}, C_7H_6I requires 216.9514), 185 (*M* − I, 11), 143 (59), 129 (70), 117 (83), 115 (15), 95 (28) and 90 (65).

2′,3′-Dihydro-3-methylidenespiro[cyclopentane-1,1′-indene] 35

A solution of the aryl iodide **33** (0.250 g, 0.80 mmol), palladium(II) acetate (1.8 mg, 1 mol %), triphenylphosphine (8.38 mg, 4 mol %) and silver(II) carbonate (0.221 g, 0.80 mmol) in dry acetonitrile (10 cm^3) was stirred at room temperature for 48 h under an atmosphere of nitrogen. The resulting mixture was filtered through Celite and the solvent removed under reduced pressure to leave a brown residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (pentane) to give the *spirocycle* **35** (88 mg, 60%) as a colourless oil; ν_{max}/cm^{-1} (film) 3069, 3020, 2940, 2857, 1642, 1477, 1456, 1435, 910, 878 and 756; δ_H(270 MHz) 7.35–7.05 (4 H, m, 4 × Ar*H*), 5.00 (2 H, br s, C=C*H*$_2$) and 2.99–1.88 (10 H, complex series of m, 5 × C*H*$_2$); δ_C(68 MHz) 152.0 (=*C*–), 149.8 (=*C*–), 143.7 (=*C*–), 128.3 (=*C*H), 126.4 (=*C*H), 124.4 (=*C*H),

122.2 (=CH), 105.9 (=CH_2), 54.9 (quat. C), 46.6 (CH_2), 39.0$_1$ (CH_2), 38.9$_6$ (CH_2), 31.6 (CH_2) and 30.4 (CH_2); *m/z* 184.1260 (68%) (*M*, $C_{14}H_{16}$ requires 184.1252), 169 (72) (*M* − CH_3), 143 (46), 128 (100), 116 (17) (*M* − C_5H_8), 91 (28) and 65 (6).

7-Phenyl-5-methylidenehept-1-ene 34

A solution of the iodide **33** (0.250 g, 0.80 mmol) in dry deoxygenated THF (5 cm^3) was injected dropwise (syringe) over 1 min to a stirred green solution of sodium cobalt(I) salophen (0.598 g, 1.60 mmol) in dry deoxygenated THF (120 cm^3) in the dark under an atmosphere of nitrogen. The reaction mixture was then stirred for 3 h in the dark under an atmosphere of nitrogen. The solution was filtered under reduced pressure to give a brown solid residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (ethyl acetate–light petroleum, 1 : 5) to give the *alkene* **34** (106 mg, 72%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3076, 3027, 2926, 2853, 1642, 1604, 1496, 1453, 1258, 911, 890 and 747; δ_H(270 MHz) 7.20–6.90 (5 H, m, 5 × Ar*H*), 5.80–5.66 (1 H, ddt, *J* 17.1, 10.2 and 6.2, C*H*=CH_2), 4.97–4.89 (1 H, *ca.* dd, *J* 17.1 and 1.7, CH=CH*H*), 4.87 (1 H, d, *J* 10.2, CH=C*H*H), 4.68 (2 H, s, C=CH_2), 2.68–2.62 (2 H, m, *ca.* dd, ArCH_2) and 2.25–2.05 (6 H, m, 3 × CH_2); δ_C(68 MHz) 148.6 (=*C*–), 142.2 (=*C*–), 138.4 (=CH), 128.3 (4 × =CH), 125.8 (=CH), 114.6 (CH=CH_2), 109.5 (C=CH_2), 37.9 (CH_2), 35.6 (CH_2), 34.3 (CH_2) and 32.0 (CH_2); *m/z* 186.1394 (6%) (*M*, $C_{14}H_{18}$ requires 186.1401), 144 (8), 143 (48), 141 (45), 131 (36) and 91 (100).

1-Hydroxyhex-5-en-2-one 36

A solution of hex-5-en-2-one (0.30 g, 3.06 mmol) in dry tetrahydrofuran (THF, 5 cm^3) was added dropwise to a stirred and cooled (−78 °C) suspension of diisopropylamine (0.47 cm^3 3.37 mmol), butyllithium in hexanes (1.6 mol dm^{-3}; 2.11 cm^3, 3.37 mmol) and chlorotrimethylsilane (0.70 cm^3, 5.51 mmol) in dry THF (40 cm^3) under an atmosphere of nitrogen. The resulting solution was stirred at −78 °C for 1.5 h under an atmosphere of nitrogen. The reaction mixture was allowed to warm to room temperature and then diluted with water (15 cm^3). The solution was concentrated under reduced pressure and then washed with light petroleum (2 × 30 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and then concentrated under reduced pressure to give a solution of the silyl enol ether (~ 15 cm^3 total volume). The solution was added dropwise to a stirred and cooled (0 °C) suspension of *m*-chloroperoxybenzoic acid (0.687 g, 3.98 mmol) in light petroleum (25 cm^3). The resulting suspension was allowed to warm to ambient temperature and then stirred for 3 h. The solution was filtered and then vigorously stirred for 3 h in aqueous hydrochloric acid (2 mol dm^{-3}; 50 cm^3) and diethyl ether (2 × 30 cm^3). The ether phase was retained and the aqueous phase was further extracted with diethyl ether (3 × 30 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to leave a colourless liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1 : 5) to give the *keto alcohol* **36** (0.221 g, 64%) as a colourless oil; ν_{max}/cm^{-1} (film) 3434 br, 3079, 2979, 2917, 1720, 1642, 1409, 1250, 1070, 999 and 917; δ_H(270 MHz) 5.81–5.66 (1 H, ddt, *J* 17.0, 10.4 and 6.4, C*H*=CH_2), 5.02–4.93 (2 H, m, CH=CH_2), 4.20 (2 H, s, CH_2OH), 3.50–3.05 (1 H, br s, O*H*), 2.48–2.36 (2 H, m, CH_2CO) and 2.35–2.25 (2 H, m, CH_2); δ_C(68 MHz) 209.0 (*C*=O), 136.2 (*C*H=CH_2), 115.9 (=CH_2), 68.2 (OCH_2), 37.5 (CH_2CO) and 27.5 (CH_2CH=); *m/z* 113.0631 (2%) (*M* − H, $C_6H_9O_2$ requires 113.0603), 83 (69) (*M* − OCH_3), 78 (10), 69 (28), 55 (100) and 43 (42).

1-[(*tert*-Butyldimethylsilyl)oxy]hex-5-en-2-one 37

A solution of 1-hydroxyhex-5-en-2-one (1.20 g, 0.01 mol), imidazole (1.02 g, 0.015 mol) and *tert*-butyldimethylsilyl chloride (1.66 g, 0.011 mol) in dry dimethylformamide (40 cm^3) was stirred for 14 h at room temperature under an atmosphere of nitrogen. Water (15 cm^3) was added and the solution was then extracted with diethyl ether (3 × 25 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to leave a yellow liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1 : 5) to give the *silyl ether* **37** (1.71 g, 75%) as a colourless oil; ν_{max}/cm^{-1} (film) 3080, 2955, 2896, 2858, 1722, 1642, 1472, 1436, 1362, 1162, 1110, 1006, 914, 838 and 779; δ_H(270 MHz) 5.81–5.66 (1 H, ddt, *J* 16.8, 10.3 and 6.6, C*H*=CH_2), 4.98–4.87 (2 H, m, CH=CH_2), 4.08 (2 H, s, CH_2OSi), 2.54–2.49 (2 H, m *ca.* dd, CH_2CO), 2.29–2.21 (2 H, m, CH_2), 0.84 [9 H, s, SiC(CH_3)$_3$] and 0.00 [6 H, s, Si(CH_3)$_2$]; δ_C(68 MHz) 210.2 (*C*=O), 137.0 (*C*H=CH_2), 115.1 (=CH_2), 69.3 (OCH_2), 37.4 (CH_2), 27.2 (CH_2), 25.7 (3 × CH_3), 18.1 [Si*C*(CH_3)$_3$] and −4.9 (2 × $SiCH_3$); *m/z* 213 (4%) (*M* − CH_3), 171 (69) [*M* − C(CH_3)$_3$], 105 (28), 89 (19), 75 (76) and 55 (10).

6-[(*tert*-Butyldimethylsilyl)oxy]-5-methylidenehex-1-ene 38

A stirred suspension of potassium *tert*-butoxide (1.41 g, 12.54 mmol) and methyltriphenylphosphonium bromide (4.48 g, 12.54 mmol) in dry diethyl ether (80 cm^3) was heated under reflux for 20 min, under an atmosphere of nitrogen. The resulting yellow solution was allowed to cool to *ca.* 30 °C and a solution of the 1-[(*tert*-butyldimethylsilyl)oxy]hex-5-en-2-one (2.21 g, 9.66 mmol) in dry ether (5 cm^3) was then added dropwise over 5 min, under an atmosphere of nitrogen. The mixture was heated under reflux for a further 20 min under nitrogen. Water (15 cm^3) was added and then the solution was extracted with diethyl ether (3 × 30 cm^3). The combined organic phases were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to leave a colourless liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1 : 5) to give the 1,5-*diene* **38** (1.68 g, 77%) as a colourless oil; ν_{max}/cm^{-1} (film) 3095–2845 br, 1641, 1460, 1440, 1350, 1260, 1150, 915, 840, 780 and 670; δ_H(270 MHz) 5.82–5.68 (1 H, ddt, *J* 16.8, 10.4 and 6.4, C*H*=CH_2), 5.00–4.75 (4 H, m, 2 × =CH_2), 4.00 (2 H, s, CH_2OSi), 2.20–2.00 (2 H, m, 2 × CH_2), 0.85 [9 H, s, SiC(CH_3)$_3$] and 0.00 [6 H, s, Si(CH_3)$_2$]; δ_C(68 MHz) 148.4 (*C*=CH_2), 138.8 (*C*H=CH_2), 115.1 (CH=CH_2), 109.2 (C=CH_2), 66.4 (OCH_2), 33.5 (2 × CH_2), 26.4 (3 × CH_3) 18.9 [Si*C*(CH_3)$_3$] and −4.9 [Si(CH_3)$_2$]; *m/z* 169 (*M* − C_4H_9, 33%), 127 (20), 113 (8), 75 (100) and 59 (7).

2-Methylidenehex-5-en-1-ol 39

A solution of 6-[(*tert*-butyldimethylsilyl)oxy]-5-methylidenehex-1-ene (1.68 g, 7.34 mmol) in dry THF (5 cm^3) was injected dropwise (syringe) over 1 min to a stirred solution of tetrabutylammonium fluoride (2.10 g, 8 mmol) in dry THF (40 cm^3) under an atmosphere of nitrogen. The resulting mixture was stirred at ambient temperature for 12 h under an atmosphere of nitrogen, then diluted with water (20 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic phases were dried ($MgSO_4$), filtered, and the solvent removed at reduced pressure to leave a pale yellow liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1 : 5) to give the 1,5-*dienol* **39** (0.678 g, 82%) as a colourless oil; ν_{max}/cm^{-1} (film) 3430 br, 2920–2840 br, 1641, 1440, 1260, 1000, 920, 840, 780 and 660; δ_H(270 MHz) 5.90–5.75 (1 H, ddt, *J* 16.8, 10.3 and 6.5, C*H*=CH_2), 5.08–4.89 (4 H, m, 2 × =CH_2), 4.08 (2 H, s, CH_2OH), 2.26–2.12 (4 H, m, 2 × CH_2) and 1.90–1.70 (1 H, br s, O*H*); δ_C(68 MHz) 148.2 (*C*=CH_2), 138.1 (*C*H=CH_2), 114.8 (CH=CH_2), 109.7 (C=CH_2), 65.9 (OCH_2), 32.2 (CH_2) and 31.9 (CH_2); *m/z* 94.0767 (21%) (*M* − H_2O, C_7H_{10} requires 94.0782), 81 (65), 79 (100), 71 (18), 70 (32), 57 (49) and 51 (15).

2-Bromo-1-ethoxyethyl 2-methylidenehex-5-enyl ether 40

A solution of the 2-methylidenehex-5-en-1-ol (0.350 g, 3.13 mmol) in dry dichloromethane (10 cm^3) was added dropwise

over 5 min to a stirred and cooled (0 °C) suspension of *N*-bromosuccinimide (0.590 g, 3.28 mmol) and ethyl vinyl ether (0.34 cm^3, 3.58 mmol) in dry dichloromethane (20 cm^3) under an atmosphere of nitrogen. The resulting suspension was allowed to warm to ambient temperature and then stirred for 48 h under nitrogen. The solution was concentrated under reduced pressure and diluted with light petroleum (60 cm^3). The resulting suspension was filtered, and then the solvent was removed under reduced pressure to leave a colourless liquid. The liquid was purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:5) to give the *bromoacetal* **40** (0.650 g, 79%) as a colourless oil; ν_{max}/cm^{-1} (film) 3070–2950 br, 1740, 1641, 1450, 1420, 1375, 1350, 1120, 1060, 990, 900 and 680, δ_H(270 MHz) 5.83–5.68 (1 H, ddt, *J* 16.8, 10.2 and 6.3, C*H*=CH_2), 5.00–4.83 (4 H, m, 2 × =CH_2), 4.63–4.57 (1 H, m, C*H*OEt), 4.06–3.83 (2 H, m, OCH_2), 3.69–3.54 (2 H, m, OCH_2CH_3), 3.33–3.29 (2 H, *ca.* t, *J* 5.6, CH_2Br), 2.18–2.05 (4 H, m, 2 × CH_2) and 1.17 (3 H, t, *J* 7.0, OCH_2CH_3); δ_C(68 MHz) 145.5 (=C–), 138.0 (=CH), 114.6 (CH=CH_2), 111.3 (C=CH_2), 101.4 (CO_2), 67.8 (OCH_2), 62.4 (OCH_2), 32.5 (CH_2), 31.8 (2 × CH_2) and 15.1 (CH_3); *m/z* 150.9733 (22%) (*M* − $C_7H_{11}O$, C_4H_8OBr requires 150.9751), 129 (46), 103 (57), 95 (23), 73 (100) and 55 (16).

{5-(3-Ethoxy)-2-oxaspiro[4.4]nonan-7-ylmethyl}(pyridinio)-cobaloxime 41

A stirred suspension of cobalt(II) chloride hexahydrate (0.354 g, 1.49 mmol), dimethylglyoxime (0.345 g, 2.98 mmol) and dry methanol (20 cm^3) was deoxygenated by bubbling nitrogen gas through the solution for 30 min at room temperature. The solution was cooled (0 °C) and then pyridine (0.12 cm^3, 1.49 mmol) was added followed by the addition of aqueous sodium hydroxide (10 mol dm^{-3}; 0.60 cm^3). A dark blue solution resulted which was stirred for a further 15 min, and then sodium borohydride (57 mg, 1.49 mmol) was added in one portion under an atmosphere of nitrogen. A deoxygenated solution of the bromoacetal **40** (0.313 g, 1.19 mmol) in dry methanol (5 cm^3) was added and the mixture was stirred for 3 h at room temperature under a nitrogen atmosphere. The resulting crude reaction mixture was adsorbed onto silica gel and then purified by chromatography over silica gel (ethyl acetate) to give the *pyridinio complex* **41** (198 mg, 47%), a *ca.* 4:3 mixture of diastereoisomers, as an orange powder, mp (dec.) > 85 °C; λ_{max}/nm 231 (ε 12 580) and 294 (ε 3370); ν_{max}/cm^{-1} ($CHCl_3$) 3060 br, 3034, 2977, 2896, 1522, 1477, 1423, 1392, 1213, 1046 and 929; δ_H(270 MHz) 8.52–8.42 (2 H, m, 2 × pyridine C*H*), 7.68–7.61 (1 H, m, pyridine C*H*), 7.25–7.16 (2 H, m, 2 × pyridine C*H*), 5.00 (1 H, dd, *J* 5.6 and 2.6, C*H*OEt), 3.68–3.52 (2 H, m, OCH_2CH_3), 3.48–3.27 (2 H, m, OCH_2), 2.05 (12 H, s, 4 × CH_3), 2.00–1.30 (8 H, br m, 4 × CH_2) and 1.12 (3 H, t, *J* 7.3, OCH_2CH_3); δ_C(68 MHz) 149.8 (2 × =CH), 149.2 (4 × N=*C*), 137.3 (=*C*H), 125.1 (2 × =*C*H), 104.6 and 104.4 (CHO_2), 63.1_3 and 63.0_6 (CH_2O), 51.3 and 49.7 (quat. C), 46.3, 45.6, 44.8 and 44.2 (all CH_2), 42.1 and 40.8 (*C*H), 38.8, 37.6, 34.1 and 33.3 (all CH_2), 15.3 (CH_3CH_2O) and 12.00 (4 × CH_3C=N); *m/z* (FAB) 551 (*M*), 472 (*M* − C_5H_5N), 427, 391, 368, 290 [Co(dmgH)$_2$ + 1], 273, 205, 154, 136 and 77.

3-Ethoxy-7-methylidene-2-oxaspiro[4.4]nonane 42

Dry benzene (50 cm^3) was deoxygenated by bubbling nitrogen gas through it for 1 h. The pyridinio cobaloxime **41** (60 mg, 0.11 mmol) was added, and the resulting orange solution was then irradiated with a UV sunlamp for 16 h under an atmosphere of nitrogen. The solvent was removed from the mixture by evaporation under reduced pressure to leave a brown solid residue. The residue was adsorbed onto silica gel and then purified by chromatography over silica gel (ethyl acetate–light petroleum, 1:5) to give the *alkene* **42** (13 mg, 65%) as a colourless liquid; ν_{max}/cm^{-1} (film) 3074, 2936, 2863, 1653, 1437, 1346, 1111, 1090, 1056, 1019, 908 and 879; δ_H(270 MHz) 5.11–5.08 (1 H, dd, *J* 5.6 and 2.6, C*H*OEt), 4.82–4.75 (2 H, br s, C=CH_2), 3.71–3.62 (1 H, m, OC*H*HMe), 3.67 (1 H, d, *J* 8.3, OC*H*HC), 3.57 (1 H, d, *J* 8.3, OCHH*C*), 3.42–3.31 (1 H, m, OCH*H*Me), 2.41–2.20 [4 H, br m, =C(CH_2)$_2$], 1.98–1.91 (1 H, dd, *J* 13.2 and 5.6, O_2CHC*H*H), 1.79–1.73 (1 H, dd, *J* 13.2 and 2.6, O_2CHCH*H*), 1.71–1.50 (2 H, m, CCH_2CH_2C=) and 1.14 (3 H, t, *J* 7.1, OCH_2CH_3); *m/z* 182.1314 (8%) (*M*, $C_{11}H_{18}O_2$ requires 182.1307), 168 (4), 149 (100), 132 (10), 71 (37) and 57 (66).

Acknowledgements

We thank the EPSRC for studentships (to A. A. and G. A. R.) and Rhône-Poulenc Rorer and Zeneca for support of these studentships *via* the CASE scheme. Dr T.-S. Kam thanks the University of Malaya for a period of study leave at Nottingham University.

References

1 R. F. Heck, *J. Am. Chem. Soc.*, 1968, **90**, 5518.
2 For an excellent recent review, see: A. de Meijere and F. E. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2379. For other reviews, see: L. E. Overman, M. M. Abelman, D. J. Kucera, V. D. Tran and D. J. Ricca, *Pure Appl. Chem.*, 1992, **64**, 1813; W. Cabri and I. Candiani, *Acc. Chem. Res.*, 1995, **28**, 2. For some recent papers, see: R. Anacardio, A. Arcadi, G. D'Anniballe and F. Marinelli, *Synthesis*, 1995, 831; J. W. Dankwardt and L. A. Flippin, *J. Org. Chem.*, 1995, **60**, 2312; R. Grigg, P. Fretwell, C. Meerholtz and V. Sridharam, *Tetrahedron*, 1994, **50**, 359; S. Ma, E. Negishi, *J. Org. Chem.*, 1994, **59**, 4730; D. J. Kucera, S. J. O'Connor and L. E. Overman, *J. Org. Chem.*, 1993, **58**, 5304; A. Ashimori, T. Matsuura, L. E. Overman and D. J. Poon, *J. Org. Chem.*, 1993, **58**, 6949; A. Ashimori and L. E. Overman, *J. Org. Chem.*, 1992, **57**, 4571; R. C. Larock, N. G. Berrios-Peña and C. A. Fried, *J. Org. Chem.*, 1991, **56**, 2615.
3 For examples, see: B. M. Trost, *Pure Appl. Chem.*, 1994, **66**, 2007; B. M. Trost and J. Dumas, *Tetrahedron Lett.*, 1993, **34**, 19; B. M. Trost and G. Kottirsch, *J. Am. Chem. Soc.*, 1990, **112**, 2816; B. M. Trost and J. M. Tour, *J. Am. Chem. Soc.*, 1988, **110**, 5231; B. M. Trost and K. Matsuda, *J. Am. Chem. Soc.*, 1988, **110**, 5233; B. M. Trost, *J. Organomet. Chem.*, 1986, **300**, 263; J. Tuji, *J. Organomet. Chem.*, 1986, **300**, 281.
4 For some examples from our own research group, see: H. Bhandal, G. Pattenden and J. J. Russell, *Tetrahedron Lett.*, 1986, **27**, 2299; V. F. Patel, G. Pattenden and J. J. Russell, *Tetrahedron Lett.*, 1986, **27**, 2303; V. F. Patel and G. Pattenden, *Tetrahedron Lett.*, 1988, **29**, 707; D. J. Coveney, V. F. Patel and G. Pattenden, *Tetrahedron Lett.*, 1987, **28**, 5949; V. F. Patel and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1987, 871; G. Pattenden, *Chem. Soc. Rev.*, 1988, **17**, 361; H. Bhandal and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1988, 1110; G. B. Gill, G. Pattenden and S. J. Reynolds, *Tetrahedron Lett.*, 1989, **30**, 3229; M. J. Begley, H. Bhandal, J. H. Hutchinson and G. Pattenden, *Tetrahedron Lett.*, 1987, **28**, 1317; H. Bhandal, V. F. Patel, G. Pattenden and J. J. Russell, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2691; V. F. Patel and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2703; H. Bhandal, A. R. Howell, V. F. Patel and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2709; A. R. Howell and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2715; D. J. Coveney, V. F. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2721; V. F. Patel, G. Pattenden and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2729; A. R. Howell and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1990, 103; D. C. Harrowven and G. Pattenden, *Tetrahedron Lett.*, 1991, **32**, 243; G. Pattenden and S. J. Reynolds, *Tetrahedron Lett.*, 1991, **32**, 259; G. Pattenden and M. Tankard, *J. Organomet. Chem.*, 1993, **460**, 237; G. B. Gill, G. Pattenden and S. J. Reynolds, *J. Chem. Soc., Perkin Trans. 1*, 1994, 369; G. Pattenden and S. J. Reynolds, *J. Chem. Soc., Perkin Trans. 1*, 1994, 379.
5 For some examples from other workers, see: M. Tada and M. Okabe, *Chem. Lett.*, 1980, 201; M. Okabe and M. Tada, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1498; J. E. Baldwin and C.-S. Li, *J. Chem. Soc., Chem. Commun.*, 1987, 166; B. P. Branchaud, M. S. Meier and M. N. Malekzadeh, *J. Org. Chem.*, 1987, **52**, 212; B. P. Branchaud, M. S. Meier and Y. L. Choi, *Tetrahedron Lett.*, 1988, **29**, 167; B. P. Branchaud and Y. L. Choi, *J. Org. Chem.*, 1988, **53**, 4638; B. P. Branchaud and G.-X. Yu, *Tetrahedron Lett.*, 1988, **29**, 6545; A. Ghosez, T. Göbel and B. Giese, *Chem. Ber.*, 1988, **121**, 1807; B. P. Branchaud and M. S. Meier, *Tetrahedron Lett.*, 1988, **29**, 3191; B.

Giese, J. Hartung, J. He, O. Hüter and A. Koch, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 325; A. J. Clark and K. Jones, *Tetrahedron Lett.*, 1989, **30**, 5485; B. P. Branchaud and M. S. Meier, *J. Org. Chem.*, 1989, **54**, 1320; A. Veit and B. Giese, *Synlett*, 1990, 166; J. E. Baldwin, M. G. Moloney and A. F. Parsons, *Tetrahedron*, 1990, **46**, 7263; B. P. Branchaud and G.-X. Yu, *Organometallics*, 1991, **10**, 3795; B. P. Branchaud and W. D. Detlefsen, *Tetrahedron Lett.*, 1991, **32**, 6273; J. E. Baldwin, R. M. Adlington and T. W. Kang, *Tetrahedron Lett.*, 1991, **32**, 7093; J. E. Baldwin, M. G. Moloney and A. F. Parsons, *Tetrahedron*, 1991, **47**, 155; B. P. Branchaud and G.-X. Yu, *Tetrahedron Lett.*, 1991, **32**, 3639; B. Giese, M. Zehnder, M. Neuburger and F. Trach, *J. Organomet. Chem.*, 1991, **412**, 415; J. Hartung and B. Giese, *Chem. Ber.*, 1991, **124**, 387; J. E. Baldwin, M. G. Moloney and A. F. Parsons, *Tetrahedron*, 1992, **48**, 9373; B. Giese, B. Carboni, T. Goebel, R. Muhn and F. Wetterich, *Tetrahedron Lett.*, 1992, **33**, 2673; B. Giese, P. Erdmann, T. Göbel and R. Springer, *Tetrahedron Lett.*, 1992, **33**, 4545; A. J. Clark and K. Jones, *Tetrahedron*, 1992, **48**, 6875; B. P. Branchaud and G.-X. Yu, *Organometallics*, 1993, **12**, 4262; B. P. Branchaud, R. M. Slade and S. K. Janisse, *Tetrahedron Lett.*, 1993, **34**, 7885; B. P. Branchaud and R. M. Slade, *Tetrahedron Lett.*, 1994, **35**, 4071.

6 A. Ali, D. C. Harrowven and G. Pattenden, *Tetrahedron Lett.*, 1992, **33**, 2851.

7 M. M. Abelman and L. E. Overman, *J. Am. Chem. Soc.*, 1988, **110**, 2328.

8 R. Pappo, D. S. Allen, R. U. Lemieux and W. S. Johnson, *J. Org. Chem.*, 1956, **21**, 478.

9 For examples of the catalytic use of cobalt reagents, see: B. P. Branchaud and Y. L. Choi, *Tetrahedron Lett.*, 1988, **29**, 6037; S. Busato, O. Tinembart, Z. Zhang and R. Scheffold, *Tetrahedron*, 1990, **46**, 3155; B. P. Branchaud and W. D. Detlefsen, *Tetrahedron Lett.*, 1991, **32**, 6273; E. R. Lee, I. Lakomy, P. Bigler and R. Scheffold, *Helv. Chim. Acta*, 1991, **45**, 86; T. Inokuchi, H. Fawafuchi, F. Aoki, A. Yoshida and S. Torii, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 595; B. B. Wayland, G. Poszmik and S. L. Mukerjee, *J. Am. Chem. Soc.*, 1994, **116**, 7943.

10 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and E. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, 41.

11 G. Costa and G. Mestroni, *J. Organomet. Chem.*, 1968, **11**, 333.

12 S. Hoff, L. Brandsma and J. F. Arens, *Recueil*, 1968, **87**, 916.

13 B. B. Snider and M. A. Dombroski, *J. Org. Chem.*, 1987, **52**, 5487.

14 S. N. Huckin and L. Weiler, *J. Am. Chem. Soc.*, 1974, **96**, 1082.

Paper 5/06947E
Received, 20*th October* 1995
Accepted 6*th December* 1995