Free Radical Reactions in Synthesis. Homolysis of Alkylcobalt Complexes in the Presence of Radical-Trapping Agents

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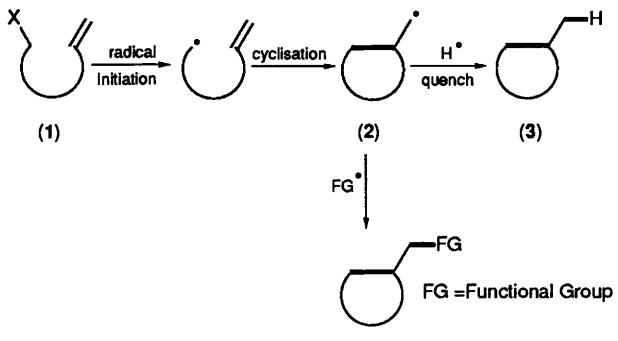
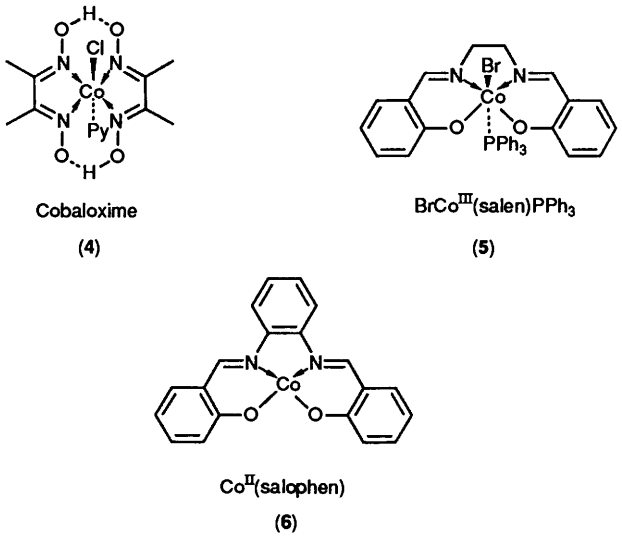
Irradiations of the alkylcobalt salophen complexes (**14**), (**21**), (**22**), and (**23**) in the presence of radical-trapping agents, *e.g.* molecular oxygen, tetramethylpiperidine oxide, nitrogen monoxide, diphenyl disulphide, diphenyl diselenide, methanesulphonyl chloride, bromotrichloromethane, or iodine, leads to oxgen- [*e.g.*, (**18**), (**19**), and (**25**)], nitrogen- [*e.g.*, (**27**) and (**28**)], sulphur/selenium-[*e.g.*, (**30**) and (**31**)] or halogen- (**34**) functionalised products. When these radical-trapping methodologies are combined with cobalt-mediated radical cyclisation reactions (Scheme 2) a powerful synthetic procedure, *i.e.* radical carbon-to-carbon bond formation with simultaneous functionalisation of the product radical centre, becomes available.

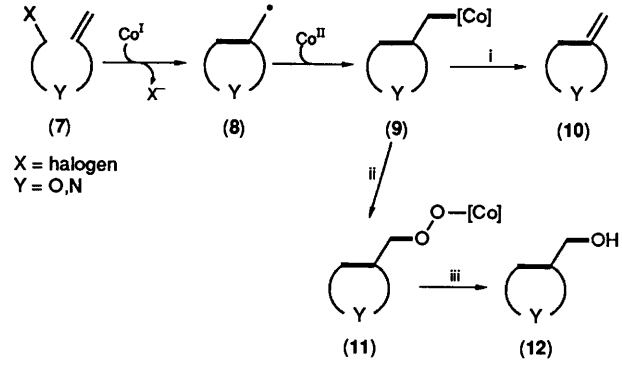
The past few years have witnessed explosive development in the design and application of free-radical-mediated reactions in all types of synthetic operation. Illustrations of the use of free radical reactions in the synthesis of carbo- and hetero-cyclic compounds have been particularly poignant.[1] The overwhelming majority of free radical cyclisation reactions, *viz.* (**1**) ⟶ (**3**), are performed under reductive conditions, with the result that ring formation is invariably accomplished at the expense of two functional groups, *i.e.* the radical precursor group X and the radical acceptor (unsaturated functionality), as illustrated in Scheme 1. The versatility of free-radical-initiated carbon-to-carbon bond-forming cyclisations of the type shown in Scheme 1 would be enhanced still further if reliable and practical procedures could be developed to introduce functionality at the product radical centre (**2**), in concert with carbon-to-carbon bond formation, by using appropriate radical-trapping methodologies. Although illustrations of free-radical trapping by, for example, oxygen,[2] nitroxides,[2] isocyanides,[3] Michael acceptors,[4] and alkyl radicals,[5] abound in the literature, the generality of these methods in synthesis has not been established.[6]



Scheme 1.

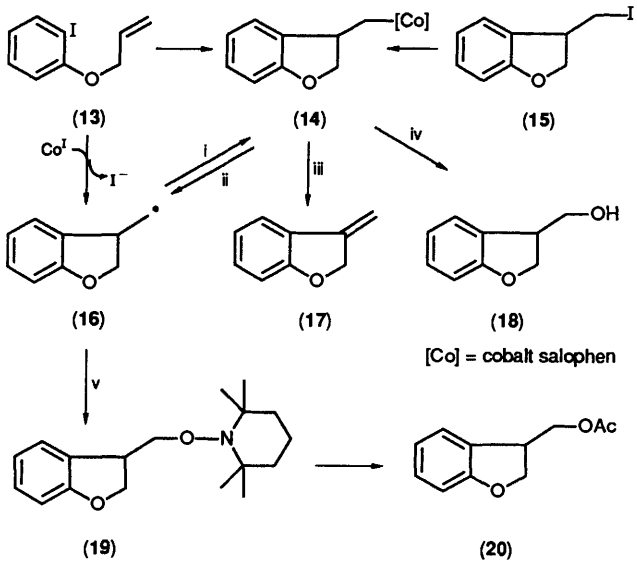
In the accompanying paper,[7] we described the use and importance of intramolecular oxidative free radical cyclisations, using cobalt complexes, *viz.* (**4**), (**5**), and (**6**), based on Vitamin B_{12}, in the synthesis of reduced heterocycles and butyrolactones (**10**). These reactions proceed *via* electron transfer from cobalt(I) species to the carbon-to-halogen bonds in the substrates (**7**), followed by: (i) intramolecular cyclisation, (ii) *in situ* trapping of the product radical centre (**8**) with Co^{II}, and (iii) dehydrocobaltation (1,2-elimination) (Scheme 2). In almost all circumstances the intermediate organocobalt complexes, *viz.* (**9**), can be isolated and characterised. In the same paper we showed that when solutions of the intermediate organocobalt complexes (**9**) were irradiated in the presence of molecular oxygen, work-up and chromatography led to





Scheme 2. *Reagents and conditions:* i, heat, – [H–Co]; ii, *hv*, O_2; iii, $NaBH_4$.

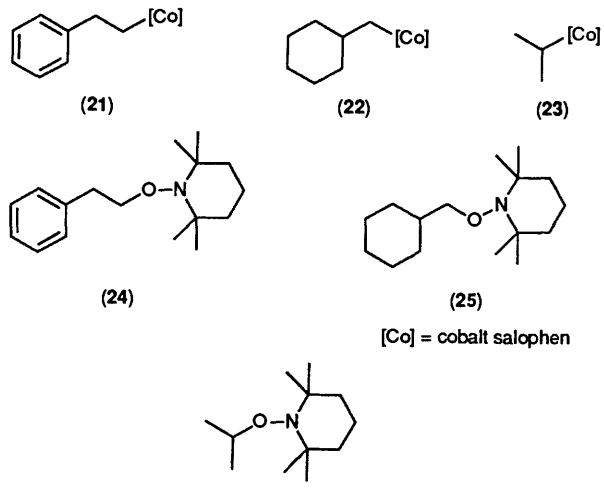
unstable peroxycobalt complexes (**11**). Reduction of these peroxycobalt complexes using alkaline sodium borohydride then provided the corresponding alcohols (**12**), *i.e.* overall radical cyclisation accompanied by functionalisation at the product radical centre by cobalt (equivalent to 'cobalt-group transfer' during radical cyclisation) and/or hydroxyl radical. As with Curran's iodine-atom-transfer method, the introduction and/or retention of functionality in the product is an enormous asset in synthesis.[1b] In this paper, we show further scope for these cobalt-group-transfer reactions in synthesis and demonstrate how the intermediate organocobalt complexes (**9**) can be used to synthesize nitrogen-, halogen-, sulphur-, selenium-, and halogen-as well as oxygen-substituted adducts of the type (**12**).[8]



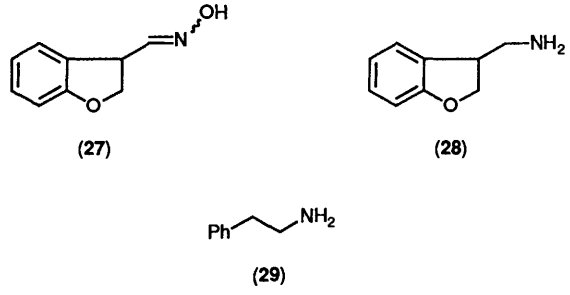
Reagents and conditions: i, Co^{II}; ii, heat or *hv*; iii, *hv*; iv, *hv*, O_2, *etc.*; v, heat, TEMPO.

Our earlier work[7] had shown that treatment of the iodoaryl allyl ether (**13**) with the cobalt salophen reagent (**6**) resulted in smooth 5-*exo*-trigonal cyclisation followed by *in situ* trapping of the product radical centre, leading to the new alkylcobalt salophen (**14**). The same complex (**14**) could also be produced by reaction between sodium cobalt(I) salophen and the iodomethyldihydrofuran (**15**). Indeed, this method was particularly simple for the preparation of the analogous model organocobalt salophens (**21**), (**22**), and (**23**).

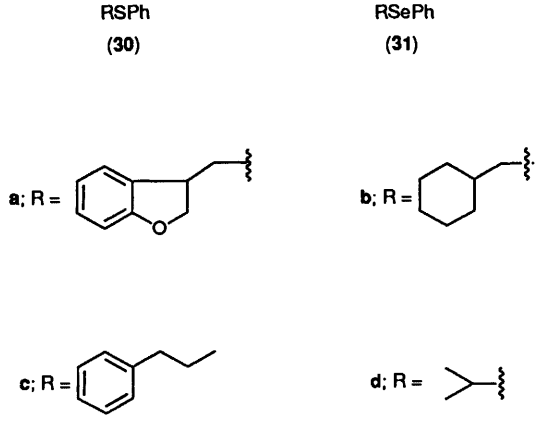
We first examined the incorporation of oxygen at the product radical centre, *viz.* (**16**), following cyclisation of compound (**13**). As we had shown earlier, irradiation of a refluxing solution of intermediate (**14**) in dichloromethane under nitrogen, using a 300 W sunlamp, led to the methylenebenzofuran (**17**) *via* 1,2-elimination, whereas irradiation in the presence of molecular oxygen, followed by reduction of the intermediate peroxycobalt complex, produced the alcohol (**18**).[7] A more practical procedure for inserting oxygenation at the product radical centre (**16**) was found to be by irradiation of intermediate (**14**) in the presence of tetramethylpiperidine oxide (TEMPO),[9] followed by reduction of the resulting hydroxylamine (**19**) with zinc in acetic acid. In this manner overall yields of 56% were realised for the conversion of intermediate (**14**) into the acetate (**20**). In a similar manner, each of the alkylcobalt salophen complexes (**21**), (**22**), and (**23**) was shown to react with TEMPO to produce the corresponding hydroxylamines (**24**), (**25**), and (**26**) respectively, in 50–75% yield.



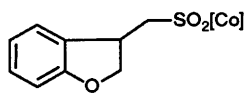
The incorporation of nitrogen at the product radical centre (**16**) resulting from cyclisation of the allyl ether (**13**) was readily accomplished when a solution of the cobalt salophen (**14**) in dimethylformamide (DMF) containing triethylamine was irradiated in the presence of nitrogen monoxide. This procedure led to a 1:1 mixture of the *Z*- and *E*-isomer of the oxime (**27**) in 73% yield, which could then be reduced to the corresponding amine (**28**). Likewise, 'oximation' of the cobalt salophen (**21**) followed by reduction provided phenylethylamine (**29**).



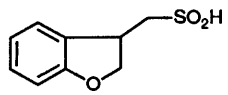
Irradiation of solutions of the alkylcobalt salophens (**14**), (**21**), (**22**), and (**23**) in the presence of diphenyl disulphide or diphenyl diselenide produced the corresponding substituted sulphides, *viz.* (**30a** and **b**) (72–85%), and selenides, *viz.* (**31a**, **c**, and **d**) (55–75%), respectively.[10a] A less practical procedure to introduce sulphur into compound (**14**) was by reaction with sulphur dioxide, followed by acidic work-up of the intermediate



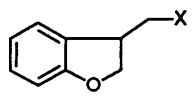
cobalt sulphone (**32**);[10b] only low yields (20% overall) of the sulphinic acid (**33**) were realised by this method. Finally, halogen could be introduced at the product radical centre (**16**) by treatment of the organocobalt intermediate (**14**) with either methanesulphonyl chloride [to afford (**34a**)], bromotrichloromethane [to (**34b**)], or iodine [to (**15**)].



(**32**)



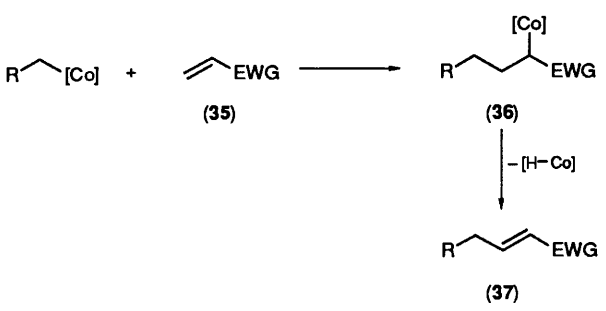
(**33**)



(**34**) **a**; X = Cl
b; X = Br

(**15**) X = I

The present studies have served to emphasise the versatility of cobalt-mediated radical reactions in the synthesis of oxygen-, nitrogen-, sulphur-, selenium-, and halogen-functionalised molecules. Irradiation of the same organocobalt complexes (**14**), (**21**), (**22**), and (**23**) in the absence of the aforementioned trapping agents produces only products resulting from elimination of cobalt hydride, *e.g.* compund (**17**). In the following paper we describe the reactions between the same alkylcobalt(III) salophens and deactivated alkenes (**35**) which lead to new alkene products (**37**) resulting from radical (Michael) addition followed by dehydrocobaltation from the organocobalt intermediates (**36**) (Scheme 3).[11]



EWG = electron-withdrawing group

Scheme 3. i, heat, *hν* (sunlamp).

Experimental

For general experimental details see ref. 7.

Preparation of Alkylcobalt(III) *Pyridinato Salophen Complexes. General Procedure.*—The alkylcobalt complexes were prepared by a modification of Marzilli's procedure.[12] A suspension of cobalt(II) salophen (373 mg, 1.00 mmol) in deoxygenated methanol (55 ml) was treated under nitrogen with a solution of sodium borohydride (171 mg, 4.50 mmol) in water (1.5 ml) at 0 °C during 20 min. There was an immediate evolution of hydrogen with a simultaneous colour change from purple to green. Neat alkyl bromide (or iodide) (1.25 mmol) was added, and the mixture was then stirred at 25 °C for 24 h in the dark. The brown solution was evaporated *in vacuo* to a quarter of its original volume and was then diluted with water (30 ml) to induce crystallisation of the base-free (5-co-ordinate) compound, RCo(salophen). The black solid was finally converted into the 6-co-ordinate species by either: (i) *recrystallisation.* The base-free compound (0.5 g) was dissolved in pyridine (20 ml) and the solution was then diluted with water until the dark green solution became turbid. The mixture was kept at room temperature in the dark for 24–48 h to give the alkylcobalt complex, or (ii) *chromatography.* The base-free solid was purified by chromatography (Alumina; 5% pyridine in dichloromethane) according to Kochi's procedure.[9] The product solution was diluted with hexane and evaporated *in vacuo* (dark; < 30 °C) to give the alkylcobalt complex.

Phenethylcobalt(III) *Pyridinato Salophen Complex* (**21**).—By the general procedure, phenethyl iodide (1.36 g, 5.86 mmol) was treated with sodium cobalt(I) salophen (4.69 mmol), and then treated with aqueous pyridine. Recrystallisation gave the complex (1.66 g, 63.6%) as a maroon solid, m.p. 151–153 °C (decomp.); $\nu_{max}(CHCl_3)$ 1 605s, 1 575s, 1 435w, 1 370w, 1 330m, 1 150m, and 910s cm^{-1}; λ_{max}(EtOH) 238, 306, 400, and 464 nm; δ_H 9.4 (br s, 2 × pyH), 8.6 (2 × CH=N), 7.9 (m, pyH), 7.6–7.0 (m, 16 × ArH), 6.6 (m, 2 × pyH), 3.5 (t, *J* 9.1 Hz, CH_2Ph), and 2.0 (t, *J* 9.1 Hz, CH_2Co); δ_C(100.62 MHz) 168.8, 144.4, 142.3, and 119.6 (C); 154.5, 149.8, 136.3, 134.3, 128.3, 128.0, 126.6, 124.9, 124.2, 124.0, 114.4, and 114.3 (CH); and 38.6 and 26.5 (CH_2) [*m/z* (FAB) $(MH - py)^+$, 479. $C_{28}H_{24}CoN_2O_2$ requires *m/z*, 479].

Cyclohexylmethylcobalt(III) *Pyridinato Salophen Complex* (**22**).—By the general procedure cyclohexylmethyl iodide (2.00 g, 8.93 mmol) was treated with sodium cobalt(I) salophen (8.93 mmol). The crude product was purified by chromatography, to give the alkylcobalt complex (4.00 g, 82%) as a black, powdery solid, m.p. 165–168 °C (from CH_2Cl_2–hexane); $\nu_{max}(CHCl_3)$ 3 005s, 2 940s, 1 605s, 1 575s, 1 440s, 1 370s, 1 335s, 1 130s, 965m, and 845m cm^{-1}; δ_H(400 MHz) 8.6 (app. d, *J* 4.3 Hz, 2 × pyH), 8.5 (2 × CH=N), 7.9–7.8 (m, 2 × ArH), 7.6 (tt, *J* 1.6 and 7.6 Hz, pyH), 7.3–7.2 (m, 10 H, 9 × ArH and pyH), 6.8–6.6 (m, 2 × ArH), 3.1 (d, *J* 5.7 Hz, CH_2Co), 1.7–1.4 (m, 2 × ring CH_2), 1.0–0.9 (m, 4 × ring CH_2), and 0.2 (m, CH); δ_C(100.62 MHz) 168.60, 144.71, and 119.84 (C); 154.97, 149.54, 135.00, 134.11, 133.91, 126.61, 124.37, 115.28, 114.28, and 41.75 (CH); and 33.14, 26.48, and 26.41 (CH_2) [*m/z* (FAB) $(M - py)^+$, 470. $C_{27}H_{27}CoN_2O_2$ requires *m/z* 470].

Isopropylcobalt(III) *Pyridinato Salophen Complex* (**23**).—By the general procedure isopropyl iodide (500 mg, 2.94 mmol) was treated with the cobalt(I) reagent (1.00 mmol), and then the crude product was recrystallised from aq. pyridine to give a mixture of two isomers of the complex (654 mg, 56.2%) as a black, crystalline solid, $\nu_{max}(CHCl_3)$ 3 660w, 3 400br w, 2 950m, 2 840m, 1 605s, 1 570s, 1 430s, 1 370s, 1 250s, 1 210m, 950w, and 660s cm^{-1}; λ_{max}(EtOH) 250, 390, and 474 nm; δ_H(250 MHz) (first isomer) 8.7 (2 × CH=N), 8.6 (br s, 2 × pyH), 8.0 (m, 2 × ArH), 7.7–7.0 (m, 11 × ArH), 6.7 (dt, *J* 1.1 and 6.7 Hz, 2 × ArH), 4.2 (septet, *J* 6.6 Hz, CHCo), and −0.4 (d, *J* 6.5 Hz, 2 × Me); (second isomer) 8.3 (2 × CH=N), 8.1 (br s, 2 × pyH), 7.9 (m, 2 × ArH), 7.7–7.0 (m, 11 × ArH), 6.5 (dt, *J* 1.1 and 6.7 Hz, 2 × ArH), 3.1 (septet, *J* 6.2 Hz, CHCo), and 0.7 (d, *J* 6.2 Hz, 2 × Me); δ_C(100.62 MHz) (first isomer) 166.5, 143.1, and 119.5 (C); (second isomer) 168.38, 145.15, and 119.76 (C); (both isomers) 156.9, 155.58, 151.8 (2 C), 135.03 (4 C), 134.17 (2 C), 133.95, 127.3, 126.8, 125.36, 124.32, 115.64, 115.50, and 114.56 (CH); and (first isomer) 77.41 and (second isomer) 28.54 (CHCo); (isomer ratio calculated from ^{13}C NMR spectroscopy was *ca.* 1:4) [*m/z* (FAB) $(MH - py)^+$, 417. $C_{23}H_{22}CoN_2O_2$ requires *m/z*, 417].

Irradiation of Alkylcobalt(III) *Pyridinato Salophen Complexes. General Procedure.*—All solvents were dried, redistilled, and

deoxygenated with nitrogen before use. A 300 W visible-light sunlamp with a tungsten filament was used for irradiation at a distance of 2 ft.* A stirred solution of the alkylcobalt complex (1.00 mmol) and the radical-trapping reagent (1.00–2.00 mmol) in either dichloromethane or DMF (20–80 ml) was heated and irradiated (*d* 25–30 cm) through Pyrex, under nitrogen. The progress of the reaction was monitored by TLC analysis of samples taken at various times. The solvent was evaporated off *in vacuo* and the residue was then purified by column chromatography.

Thermolysis of Alkylcobalt(III) *Salophen Complexes. General Procedure.*—A solution of the alkylcobalt complex (1.00 mmol) and the radical-trapping reagent (1.00–2.00 mmol) in deaerated pyridine (40 ml) was heated under reflux for 24–48 h, under nitrogen. The mixture was acidified with 2M-hydrochloric acid and then extracted with diethyl ether (5 × 20 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo*, and the residue was then purified by column chromatography.

1-[(2,3-*Dihydrobenzofuran*-3-*yl*)*methoxy*]-2,2,6,6-*tetramethylpiperidine* (**19**).—A solution of the alkylcobalt complex (**14**) (351 mg, 600 μmol) and TEMPO (103 mg, 666 μmol) in dichloromethane (55 ml) was irradiated for 30.5 h, as described in the general procedure. The brown mixture was quenched in brine (150 ml) and then extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with water (20 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The brown, oily residue was purified by chromatography (silica; light petroleum ⟶ 1:40 diethyl ether–light petroleum) to give: (i) the olefin (**17**) (25 mg, 3%) (eluted first) as an oil, whose spectral data were identical with those obtained previously,[7] and (ii) the *hydroxylamine* (**19**) (112.5 mg, 65%) as a viscous oil, ν_{max}(film) 2 980s, 1 610s, 1 480s, 1 375m, and 740m cm^{-1}; δ_H 7.2 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.7 (dd, *J* 8.6 and 9.7 Hz, OC*H*H), 4.3 (dd, *J* 5.7 and 9.7 Hz, OCH*H*), 3.9 (m, CH_2ON), 3.8 (m, ArC*H*), 1.4 (br s, 3 × CH_2), and 1.3 (br s, 4 × Me); (Found: C, 74.6; H, 9.5; N, 5.0%; M^+, 289.2041. $C_{18}H_{27}NO_2$ requires C, 74.7; H, 9.4; N, 4.8%; *M*, 289.2041).

(2,3-*Dihydrobenzofuran*-3-*yl*)*methyl Ethanoate* (**20**).—Activated zinc dust (300 mg, 4.62 mmol) was added portionwise, at 25 °C, to a stirred solution of the hydroxylamine (**19**) (78 mg, 270 μmol) in glacial acetic acid (10 ml), under nitrogen. The mixture was heated at 100 °C for 41.5 h, then quenched in water (30 ml) and extracted with diethyl ether (4 × 20 ml). The combined extracts were washed successively with saturated aq. sodium hydrogen carbonate (2 × 5 ml) and water (5 ml), then dried ($MgSO_4$), and concentrated under reduced pressure to leave a yellow oil. Purification of the oil by passage through a short pad of silica (1:3 diethyl–light petroleum) gave the *acetate* (**20**) (44.7 mg, 86.5%) as an oil, ν_{max}($CHCl_3$) 2 950m, 2 900m, 1 730s, 1 600s, 1 460m, 1 370m, and 1 020m cm^{-1}; δ_H 7.2 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.6 (dd, *J* ~ 9.2 Hz, OC*H*H), 4.35 (dd, *J* 5.5 and 9.2 Hz, OCH*H*), 4.3 (dd, *J* 5.4 and 17.5 Hz, C*H*HOAc), 4.1 (dd, *J* 6.7 and 17.5 Hz, CH*H*OAc), 3.8 (m, ArC*H*), and 2.1 (Ac) (Found: C, 68.7; H, 6.5%; M^+, 192.0780. $C_{11}H_{12}O_3$ requires C, 68.7; H, 6.3%; *M*, 192.0786).

2,2,6,6-*Tetramethyl*-2-*phenylethoxypiperidine* (**24**).—A solution of the phenethylcobalt(III) salophen complex (**21**) (48 mg, 86.2 μmol) and TEMPO (13.4 mg, 86.2 μmol) in pyridine (12 ml) was heated according to the general procedure for 19 h. The mixture was quenched with water (50 ml), and then extracted with diethyl ether (3 × 10 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo*, and the oily residue was then purified by chromatography (silica; light petroleum) to give the *hydroxylamine* (**24**) (14.6 mg, 65.2%) as an oil, ν_{max}($CHCl_3$) 2 920s, 1 595w, 1 445m, 1 355m, 1 130m, 1 030m, and 955w cm^{-1}; δ_H 7.2 (br s, Ph), 3.9 (t, *J* 6.9 Hz, CH_2O), 2.8 (t, *J* 7.0 Hz, CH_2Ph), 1.4 (br s, 6 H, 3 × CH_2), and 1.1 (br s, 4 × Me) (Found: M^+, 261.2077. $C_{17}H_{27}NO$ requires *M*, 261.2092).

Irradiation of a stirred solution of the alkylcobalt complex (**21**) (48.0 mg, 86.2 μmol) and TEMPO (20.0 mg, 128.2 μmol), by the general procedure, led to the same hydroxylamine (11.3 mg, 50.4%).

Phenethyl Acetate.—Activated zinc dust (40 mg, 615 μmol) was added portionwise to a solution of the hydroxylamine (**24**) (11.5 mg, 44.1 μmol) and the resulting suspension was then heated at 100 °C for 23.5 h. The mixture was quenched with water (20 ml) and was then extracted with diethyl ether (3 × 5 ml). The combined extracts were washed successively with saturated aq. sodium hydrogen carbonate (2 × 10 ml) and water (10 ml) and were then dried ($MgSO_4$), and evaporated *in vacuo* to leave an oil, which was then purified by chromatography (silica; 1:5 diethyl ether–light petroleum) to give the acetate (5.2 mg, 72.2%) as an oil, ν_{max}($CHCl_3$) 2 920s, 1 725s, and 1 600w cm^{-1}; δ_H 7.3 (br s, Ph), 4.3 (t, *J* 7.1 Hz, CH_2OAc), 2.9 (t, *J* 7.2 Hz, CH_2Ph), and 2.0 (Ac) [Found: $(M - AcOH)^+$, 104.0642. C_8H_8 requires *m/z*, 104.0626], which data were consistent with those obtained from authentic material.†

Cyclohexylmethoxy-2,2,6,6-*tetramethylpiperidine* (**25**).—A solution of the cyclohexylmethylcobalt complex (**22**) (549 mg, 1.00 mmol) and TEMPO (20 3 mg, 1.30 mmol) in dichloromethane (120 ml) was irradiated for 48 h, according to the general procedure. Work-up, followed by chromatographic purification (silica; 1:5 diethyl–light petroleum) gave the *hydroxylamine* (**25**) (156 mg, 52%) as an oil, ν_{max}(film) 2 940s, 1 450m, 1 370m, 1 040m, and 710w cm^{-1}; δ_H 3.6 (d, *J* 5.6 Hz, CH_2O) and 1.8–1.1 (m, CH, 8 × ring CH_2, and 4 × Me) (Found: M^+, 253.2413. $C_{16}H_{31}NO$ requires *M*, 253.2405).

Isopropoxy-2,2,6,6-*tetramethylpiperidine* (**26**).—A solution of TEMPO (21 mg, 133 μmol) and the isopropylcobalt(III) salophen complex (**23**) (66 mg, 133 μmol) in pyridine (10 ml) was heated for 28 h, according to the general procedure. The mixture was quenched with water (80 ml) and then extracted with diethyl ether (5 × 15 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo* and the resulting oily residue was then purified by chromatography (silica; light petroleum) to give the *hydroxylamine* (**26**) (20.0 mg, 75.5%) as an oil; ν_{max}($CHCl_3$) 2 920s, 1 450m, 1 375m, 1 130m, 1 110m, and 955m cm^{-1}; δ_H 4.0 (m, CH) and 1.4–1.1 (m, 6 × Me and 3 × CH_2) (Found: M^+, 199.1947. $C_{12}H_{25}O$ requires *M*, 199.1936).

Oximation of Alkylcobalt(III) *Pyridinato Salophen Complexes. General Procedure.*—A mixture of nitric oxide (purified by passage through potassium hydroxide pellets) and nitrogen gases was bubbled through a stirred solution of the alkylcobalt complex (1.00 mmol) and dry triethylamine (1.00 mmol) in dry, redistilled, deoxygenated DMF (60 ml) during 20–30 h, whilst the solution was simultaneously irradiated by a 300 W lamp. The resulting brown solution was quenched with brine (100 ml), and then extracted with diethyl ether (5 × 30 ml). The combined extracts were washed with water 3 × 40 ml), then dried ($MgSO_4$), and evaporated *in vacuo* to leave a brown residue, which was purified by column chromatography.

* 1 ft = 3.048 × 10^{-1} m.

† Commercial sample, Aldrich Chem. Co., Ltd.

2,3-*Dihydrobenzofuran*-3-*carbaldehyde Oxime* (**27**).—By the general procedure, a solution of the alkylcobalt complex (**14**) (1.00 g, 1.709 mmol) and triethylamine (237 μl, 1.709 mmol) in DMF (100 ml) was irradiated, in the presence of nitric oxide, for 26 h. The residue obtained after work-up was purified by chromatography (silica; 1:4 diethyl ether–light petroleum) to give the *oxime* (**27**) (203.7 mg, 73%) as a 1:1 mixture of the *Z*- and *E*-isomer, which was recrystallised from diethyl ether–light petroleum as crystals, m.p. 96–98 °C; ν_{max}($CHCl_3$) 3 575s, 3 300br s, 2 880s, 1 600s, 1 455m, 1 320m, 1 100m, 980m, and 910m cm^{-1}; δ_H(*E*-isomer) 8.7 (br s, OH), 7.2 (m, 2 × ArH and C*H*=NOH), 6.9 (m, 2 × ArH), 5.0–4.7 (m, OCH_2), and 4.4 (m, ArC*H*); δ_C(100.62 MHz) 160.1, 151.8, 129.1, 126.4, 125.0, 121.0, 109.8, 74.3, and 38.8 (Found: C, 66.1; H, 5.6; N, 8.6%; M^+, 163.0638. $C_9H_9NO_2$ requires C, 66.2; H, 5.6; N, 8.6%; *M*, 163.0633).

Reduction of Oximes to Amines. General Procedure.—Method (i). The oxime was reduced with sodium metal in propan-1-ol by the procedure described by Sugden and Patel.[13]

Method (ii). Lithium aluminium hydride (3.5 mmol) was added portionwise to a solution of the oxime (1.00 mmol) in dry diethyl ether (20 ml), under nitrogen, during 30 min at room temperature. A steady evolution of hydrogen gas followed, and the mixture was then heated under reflux for 36 h. The mixture was diluted with diethyl ether (20 ml) and was then carefully quenched sequentially with water (10 ml) and with 20% aq. sodium hydroxide (20 ml). The mixture was extracted with diethyl ether (4 × 20 ml) and the amine was isolated by extraction with 2M-hydrochloric acid (2 × 30 ml). The aqueous phase was neutralised with saturated aq. sodium hydrogen carbonate and was then re-extracted with diethyl ether (4 × 20 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo*.

(2,3-*Dihydrobenzofuran*-3-*yl*)*methylamine* (**28**).—The oxime (**27**) (21.0 mg, 128.8 μmol) was reduced by lithium aluminium hydride according to the general procedure, to give the amine (**28**) (11.6 mg, 60%) as a very unstable oil; ν_{max}($CHCl_3$) 3 300br s, 3 030br s, and 1 605m cm^{-1}; δ_H 7.7–7.1 (m, 2 × ArH), 6.9–6.8 (m, 2 × ArH), 4.6–4.3 (m, OCH_2), and 2.9 (app. d, *J* 6.2 Hz, CH_2NH_2).

Phenethylamine (**29**).—A solution of the phenethylcobalt(III) salophen (**21**) (205 mg, 369 μmol) and triethylamine (30 mg, 297 μmol) in DMF (25 ml) was irradiated in the presence of nitric oxide for 21 h, as described in the general procedure. A brown, oily residue was obtained after work-up, which was then purified by chromatography (silica; 1:10 diethyl ether–light petroleum) to give phenylacetaldehyde oxime (36.6 mg, 78%) as a white, crystalline solid, m.p. 80–81 °C (1:1 mixture of *E*- and *Z*-isomer); ν_{max}($CHCl_3$) 3 570s, 3 320br s, and 1 600w cm^{-1}; δ_H 8.3 (br s, 2 × OH), 7.5 (t, *J* 6.3 Hz, C*H*=NOH), 7.3 (m, 2 × Ph), 6.9 (t, *J* 5.4 Hz, C*H*=NOH), 3.7 (d, *J* 5.3 Hz, CH_2Ph), and 3.5 (d, *J* 6.3 Hz, CH_2Ph) (Found: M^+, 135.0658. C_8H_9NO requires *M*, 135.0684).

The oxime (405 mg, 3.00 mmol) was reduced with lithium aluminium hydride, according to the general procedure. Work-up and distillation (Kugelrohr) gave the amine (251 mg, 69%) as an oil; b.p. 100–105 °C/16 mmHg (lit.,[14] b.p. 197–200 °C).

3-(*Phenylthiomethyl*)-2,3-*dihydrobenzofuran* (**30a**).—A solution of the alkylcobalt(III) salophen complex (**14**) (585 mg, 1.00 mmol) and diphenyl disulphide (872 mg, 4.00 mmol) in dichloromethane (70 ml) was irradiated for 24 h, according to the general procedure. The mixture was diluted with dichloromethane (100 ml), and was then washed successively with dil. aq. sodium hydroxide (2M; 2 × 30 ml) and water (2 × 30 ml). The dried ($MgSO_4$) organic phase was evaporated *in vacuo* and the residue was then purified by chromatography (silica; 1:100 diethyl ether–light petroleum) to give the title sulphide (206 mg, 85%) as a viscous, yellow oil, ν_{max}(film) 3 060m, 2 950w, 1 600m, 1 485s, 1 235m, 970w, and 690s cm^{-1}; δ_H 7.2 (m, 7 × ArH), 6.8 (m, 2 × ArH), 4.5 (m, OCH_2), 3.6 (m, ArC*H*), and 3.1 (m, CH_2S); δ_C(20.15 MHz) 160.1, 135.6, and 115.2 (C); 129.9 (2 C), 129.0, 128.8 (2 C), 126.6, 124.5, 120.5, 109.8, and 41.7 (CH); and 76.0 and 38.9 (CH_2) (Found: C, 74.4; H, 6.0; S, 12.8%; M^+, 242.0760. Calc. for $C_{15}H_{14}OS$: C, 74.3; H, 5.8; S, 13.2%; *M*, 242.0762), which data were consistent with the literature.[15]

3-(*Phenylselenomethyl*)-2,3-*dihydrobenzofuran* (**31a**).—A solution of the alkylcobalt(III) salophen complex (**14**) (585 mg, 1.00 mmol) and diphenyl diselenide (468 mg, 1.50 mmol) in dichloromethane (70 ml) was irradiated for 20.5 h, according to the general procedure. The solvent was removed *in vacuo* and the solid residue was then purified by chromatography (silica; 1:100 ⟶ 1:15 diethyl ether–light petroleum) to give the *title selenide* (215.6 mg, 74.6%) as a low melting, yellow solid; m.p. 34–36 °C (from light petroleum–diethyl ether); ν_{max}(film) 3 060w, 2 940w, 1 605w, 1 585w, 1 485s, 1 240s, 970w, and 695m cm^{-1}; δ_H 7.5 (m, 2 × ArH), 7.2 (m, 5 × ArH), 6.8 (m, 2 × ArH), 4.6 (dd, *J* ~ 8.8 Hz, OC*H*H), 4.4 (dd, *J* 6 and 8.8 Hz, OCH*H*), 3.6 (m, ArC*H*), 3.3 (dd, *J* 4 and 10.8 Hz, C*H*HSe), and 2.9 (dd, *J* 10.4 and 11.6 Hz, CH*H*Se); δ_C(100.62 MHz) 160.2, 129.7, and 129.6 (C); 133.2 (2 C), 129.2, 128.8 (2 C), 127.3, 124.3, 120.4, 109.9, and 42.5 (CH); and 76.8 and 31.9 (CH_2) (Found: C, 62.4; H, 4.8%; M^+, 290.0195. $C_{15}H_{14}OSe$ requires C, 62.3; H, 4.9%; *M*, 290.0210).

Phenyl Phenethyl Selenide (**31c**).—A solution of the phenethylcobalt complex (**21**) (557 mg, 1.00 mmol) and diphenyl diselenide (374.4 mg, 1.20 mmol) in dichloromethane (80 ml) was irradiated for 24 h, according to the general procedure. The solvent was evaporated off and the residue was then purified by chromatography (silica; light petroleum) to give the selenide (194 mg, 61.5%) as a yellow oil; ν_{max}(film) 1 600w and 1 580m cm^{-1}; δ_H 7.6–7.4 (m, 2 × ArH), 7.3–7.0 (m, 8 × ArH), and 3.2–2.9 (m, 4 H, 2 × CH_2) (Found: C, 64.5, H, 5.6%; M^+, 263.0293. Calc. for $C_{14}H_{14}Se$: C, 64.4; H, 5.4%; *M*, 263.0293), consistent with the literature data.[16]

Cyclohexylmethyl Phenyl Sulphide (**30b**).—A solution of the alkylcobalt complex (**22**) (549 mg, 1.00 mmol) and diphenyl disulphide (262 mg, 1.20 mmol) in dichloromethane (80 ml) was irradiated for 48 h, according to the general procedure. The solvent was evaporated off *in vacuo* and the residue was then purified by recrystallisation from light petroleum (to remove excess of diphenyl disulphide) followed by distillation of the mother liquor to give the sulphide (**30b**) (146 mg, 70.9%) as an oil, which rapidly turned to a yellow oil on storage at room temperature; b.p. 140–148 °C/1.3 mmHg (lit.,[17] 151–152 °C/7 mmHg); ν_{max}(film) 2 990s, 1 585m, and 730s cm^{-1}; δ_H 7.5–7.1 (m, Ph), 2.8 (d, *J* 6.3 Hz, CH_2S), 1.9–0.9 (m, CH and 5 × ring CH_2) (Found: M^+, 206.1098. Calc. for $C_{12}H_{18}S$: *M*, 206.1067).

Isopropyl Phenyl Selenide (**31d**).—A solution of the isopropylcobalt complex (**23**) (495 mg, 1.00 mmol) and diphenyl diselenide (374.4 mg, 1.20 mmol) in dichloromethane (60 ml) was irradiated for 13 h, according to the general procedure. The solvent was evaporated off *in vacuo*, and the residue was then purified by removal of the starting diphenyl diselenide by recrystallisation from light petroleum and distillation of the mother liquor under vacuum to give the title selenide (108 mg, 54%) as an oil; b.p. 165–170 °C/1.25 mmHg (Kugelrohr) (lit.,[16] 44–46 °C/0.3 mmHg); ν_{max}(film) 2 960m and 1 500m cm^{-1}; δ_H 7.6–7.3 (m, 2 × ArH), 7.3–7.2 (m, 3 × ArH), 3.4 (septet, *J* 6.7

Hz, CHSe), and 1.4 (d, J 6.8 Hz, 2 × Me) (Found: M^+, 200.0114. Calc. for $C_9H_{12}Se$: M, 200.0104).

(2,3-*Dihydrobenzofuran*-3-*yl*)*methylsulphinatocobalt*(III) *Pyridine Salophen* (**32**).—Liquid sulphur dioxide (40 ml) was condensed onto the alkylcobalt complex (**14**) (1.00 g, 1.709 mmol) at −78 °C in a thick-walled pressure vessel. The mixture was stirred at room temperature and in the dark for 44 h. The vessel was cooled to −78 °C and the excess of sulphur dioxide was then evaporated off under nitrogen at room temperature. The orange, solid residue was purified by chromatography (silica; 1:40 MeOH–$CHCl_3$) to give the title complex (650 mg, 58.6%) as a bronze solid; ν_{max} 2 950w, 1 610s, 1 580s, 1 440m, 1 339m, 1 150m, and 955w cm^{-1}; δ_H(250 MHz) 8.49 and 8.47 (CH=N), 8.2 and 8.0 (CH=N), 8.0–6.5 (m, 21 × ArH), 4.6 (dd, J ~ 9.3 Hz, OC*H*H), 4.2 (dd, J 9.3 and 7.6 Hz, OCH*H*), 4.1 (dd, J 11.5 and 13.7 Hz, C*H*HSO_2), 4.1 (m, ArC*H*), and 3.6 (dd, J 10.8 and 13.7 Hz, CH*H*SO_2); δ_C(100.62 MHz) 166.9, 159.9, 143.9, 128.9, 119.1, and 118.9 (C); 150.2, 138.0, 136.2, 135.4, 128.3, 128.1, 124.8, 124.5, 123.3, 120.3, 116.0, 115.8, 109.4, and 36.9 (CH); and 77.0 and 53.4 (CH_2) {m/z (FAB) (Co[salophen]H)$^+$, 374. $C_{20}H_{15}CoN_2O_2$ requires M, 374}.

(2,3-*Dihydrobenzofuran*-3-*yl*)*methanesulphinic Acid* (**33**).—Dil. hydrochloric acid (2M; 4 ml) was added dropwise to a red solution of the alkylsulphinatocobalt complex (**32**) (66.5 mg, 102.8 mmol) in dry tetrahydrofuran (12 ml). The mixture was stirred in the dark and under nitrogen for 22.5 h at room temperature and the solvent was then evaporated off *in vacuo* to leave the crude sulphinic acid (**33**) (5 mg), δ_H 7.3–6.7 (m, 4 × ArH), 4.7 (dd, J ~ 9.0 Hz, OC*H*H), 4.4 (dd, J 6.1 and 9.0 Hz, OCH*H*), 4.0 (m, ArC*H*), 3.8–3.5 (m, C*H*HSO_2H), and 3.2–3.0 (m, CH*H*SO_2H). Attempted purification of the residue was unsuccessful and led to complete decomposition.

3-(*Chloromethyl*)-2,3-*dihydrobenzofuran* (**34a**).—A solution of the alkylcobalt complex (**14**) (585 mg, 1.00 mmol) and methanesulphonyl chloride (844 mg, 7.37 mmol) in dichloromethane (25 ml) was irradiated for 4 h, according to the general procedure. The solvent was evaporated off and the solid residue was then purified by chromatography (silica; 1:1 diethyl ether–light petroleum) to give the chloride (**34a**) (128.5 mg, 76.3%) as a dark orange oil; ν_{max} 3 040m, 2 950m, 1 605m, 1 590s, 1 480s, 1 330w, 1 240s, and 745s cm^{-1}; δ_H 7.1 (m, 2 × ArH), 6.9 (m, 2 × ArH), 4.5 (m, OCH_2), and 4.1–3.4 (m, 3 H, ArC*H* and CH_2Cl) (Found: M^+, 168.0343. C_9H_9ClO requires M, 168.0340).

3-(*Bromomethyl*)-2,3-*dihydrobenzofuran* (**34b**).—A solution of the alkylcobalt(III) salophen complex (**14**) (585 mg, 1.00 mmol) and bromotrichloromethane (1.9 g, 10 mmol) in dichloromethane (20 ml) was irradiated for 4.5 h, according to the general procedure. The residue was purified by chromatography (silica; 1:20 diethyl ether–light petroleum) and gave the bromide (**34b**) (154.6 mg, 78.5%) as a yellow oil (which darkened on storage in air), ν_{max}(film) 2 960w, 1 600m, 1 480s, 1 235s, and 750s cm^{-1}; δ_H 7.2 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.5 (m, OCH_2), 3.7 (m, ArC*H*), and 3.5 (m, CH_2Br); δ_C 160.3 and 127.6 (C); 129.4, 124.6, 120.7, 110.2, and 34.9 (CH); and 75.9 and 44.8 (CH_2) (Found: M^+, 213.9833. Calc. for C_9H_9BrO: M, 213.9832), consistent with the literature data.[15]

3-(*Iodomethyl*)-2,3-*dihydrobenzofuran* (**15**).—A solution of the alkylcobalt complex (**14**) (585 mg, 1.00 mmol) and iodine (508 mg, 2.00 mmol) in pyridine (40 ml) was heated for 44 h, according to the general procedure. The crude material was purified by chromatography (silica; light petroleum) to give: (i) 3-methylbenzofuran (eluted first) (34 mg, 26%) as an oil, whose spectral data were consistent with those obtained previously,[7] and (ii) the iodide (**15**) (eluted second) (109 mg, 42%) as a pale yellow oil, whose spectral data were identical with those obtained previously.[7]

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