Cobalt-mediated Reactions in Synthesis. The Degradation of Carboxylic Acids to Functionalised Noralkanes *via* Acylcobalt Salophen Intermediates

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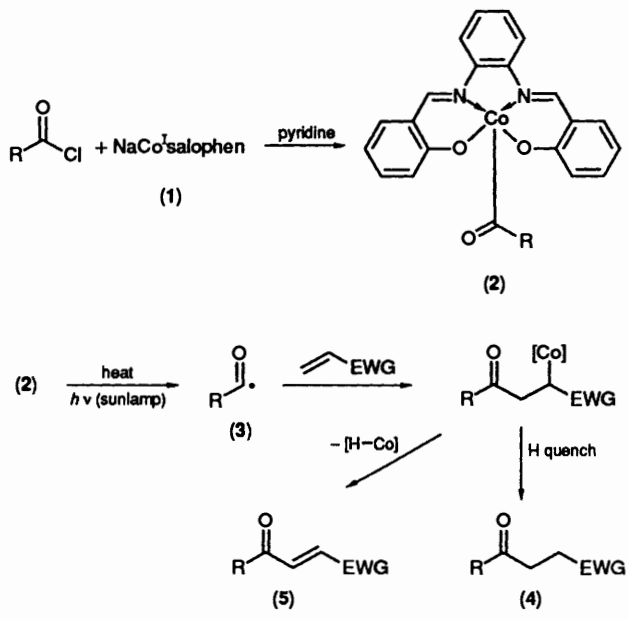
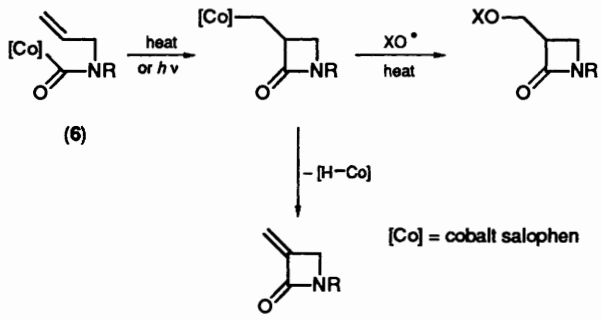
Arylmethyl- and allyl-carbonylcobalt salophen complexes, *e.g.* (**7**), (**8**), (**9**), and (**22**), readily undergo carbon-to-cobalt-bond homolysis and *in situ* decarbonylation, producing new alkyl radical centres which can be intercepted with oxygen-, nitrogen-, halogen-, sulphur-, and selenium-containing radical-trapping agents leading to functionalised noralkanes. The sequence constitutes a useful, and in some cases more flexible, variant of the classical Hunsdiecker reaction, and amounts to a cobalt equivalent of the Barton radical decarboxylation reaction of carboxylic acids *via* their corresponding thiohydroxamic esters. In a similar manner, irradiation of the oxy-substituted acylcobalt salen reagents (**25**) and (**26**) in the presence of tetramethylpiperidine oxide produces the products (**14**) and (**27**), respectively, resulting from homolysis–decarboxylation and alkyl-radical trapping. In the absence of radical-trapping agents, irradiation of (**7c**) produces (**18**), and irradiation of (**29**) leads to the but-2-enolide (**32**).

Acylcobalt salophen reagents (**2**) are conveniently synthesized from carboxylic acid chlorides by treatment with sodium cobalt(I) salophen (**1**).[1] The reagents can be prepared on a large scale from primary, secondary, and tertiary alkyl, allyl, vinyl, aryl, arylmethyl, oxy, and aminyl carboxylic acid derivatives, and all of them are brightly coloured, air-stable, crystalline materials.[2] In the accompanying paper we described the use of primary and secondary alkyl, and of aryl carbonylcobalt salophens as precursors to acyl radicals (**3**) for carrying out additions to carbon-to-carbon double bonds leading to new ketone (**4**), new alkene (**5**), and to functionalised ring systems (Scheme 1).[2] In other work we have highlighted a new synthetic approach to β-, γ-, and δ-lactams based on intramolecular cyclisation of ω-alkenyl-substituted carbamoylcobalt salophens (**6**) (Scheme 2).[3] We now describe our studies of the carbon-to-cobalt bond homolysis of a range of arylmethyl-, allyl-, and alkoxy-substituted carbonylcobalt salophen reagents and their *in situ* decarbonylation/decarboxylation. In many cases these reactions are shown to lead to new *alkyl* radical centres which can then be intercepted with oxygen-, nitrogen-, sulphur, selenium-, and halogen-containing radical-trapping agents, leading to functionalised noralkanes.[4]



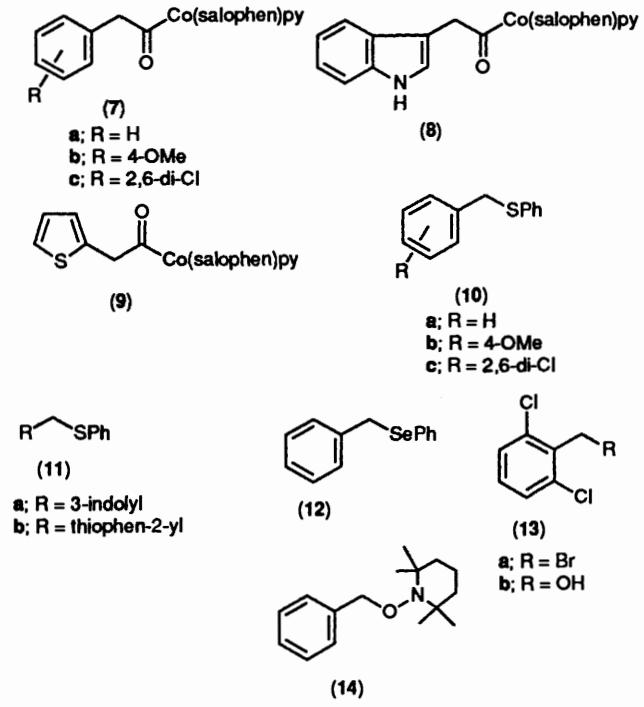
Scheme 1.



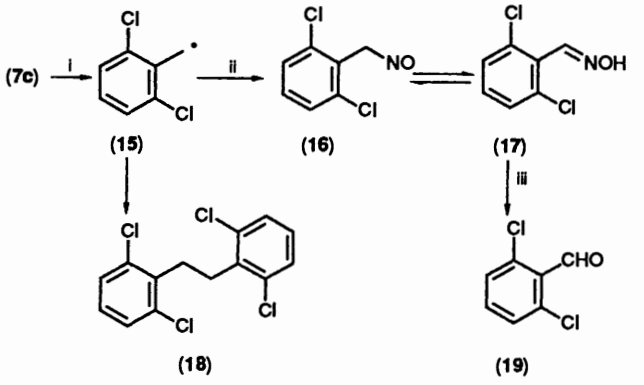
Scheme 2.

We first examined the irradiation of a series of substituted phenylacylcobalt salophen compounds, *i.e.* (**7a**), (**7b**), and (**7c**), and the heterocyclic analogues (**8**) and (**9**), in dichloromethane in the presence of diphenyl disulphide and diphenyl diselenide. Thus, irradiation of any of the phenylacylcobalt salophens (**7a–c**) in the presence of diphenyl disulphide, using light from an ordinary 300 W sunlamp, led to their clean conversion into the corresponding benzyl phenyl sulphides (**10**) in 50–65% preparative yield. In a similar manner, the indole (**8**) and the thiophene (**9**) acylcobalt reagents underwent smooth *in situ* carbon-to-cobalt bond homolyses, decarbonylations, and phenylthio-trapping reactions in the presence of diphenyl disulphide to give the phenyl sulphides (**11a**) and (**11b**), respectively. Likewise, irradiation of solutions of the acylcobalt salophens (**7**) in the presence of diphenyl diselenide produced the corresponding aryl phenyl selenides, *e.g.* (**12**), in good to excellent yield (60–80%).

Bromodecarboxylation reactions, leading to arylmethyl bromides, *e.g.* (**13a**), could be effected in the phenylacylcobalt salophens (**7**) simply by irradiation in the presence of



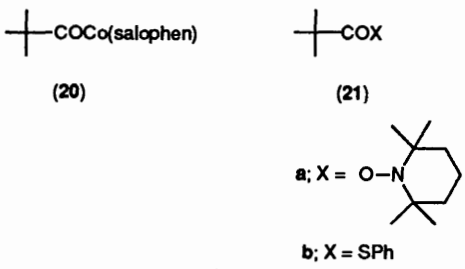
bromotrichloromethane. Furthermore, when molecular oxygen was bubbled through an irradiated and refluxing solution of 2,6-dichlorophenylacetylcobalt salophen (**7c**) in dichloromethane, an intermediate peroxycobalt complex was produced, which upon work-up by reduction with sodium borohydride led to the benzyl alcohol (**13b**) in 40% overall yield. A more satisfactory method of introducing oxygen at the product radical centre following homolysis–decarbonylation, however, was simply to irradiate solutions of the acylcobalt salophen in the presence of tetramethylpiperidine oxide (TEMPO);[5] in this manner, the phenylacetylcobalt salophen (**7a**), for example, led to the hydroxylamine (**14**) in 62% yield.



Reagents and conditions: i, *hν* (sunlamp); ii, NO; iii, H_3O^+.

Interestingly, when a solution of 2,6-dichlorophenylacetylcobalt salophen (**7c**) in dichloromethane was irradiated with a sunlamp in the presence of nitrogen monoxide, hydrolytic work-up, followed by chromatography, led to 2,6-dichlorobenzaldehyde (**19**) in 72% overall yield. The benzaldehyde (**19**) is no doubt produced from hydrolysis of the oxime tautomer (**17**) of the nitroso adduct (**16**) derived after trapping of the arylmethylene intermediate (**15**) with nitrogen monoxide.† Straightforward irradiation of the acylcobalt salophen (**7c**) in the absence of a radical trap leads only to the corresponding diarylethane (**18**).[6]

The decarbonylation reactions described above amount to a cobalt 'equivalent' of the Barton radical decarboxylation reaction of carboxylic acids *via* the corresponding thiohydroxamic ester.[7] They therefore resemble the classical Hunsdiecker reaction. In other work, Dessan and Heiba[8] have shown that phenylacetic acids undergo oxidative decarboxylation when treated with cobalt(III) acetate, leading to benzyl acetate, and Waters and co-workers[9] have demonstrated their conversion into benzaldehydes on using potassium perchlorate. Kochi's method for the preparation of alkyl halides from the homologous carboxylic acids using lithium chloride and lead tetra-acetate is also worth noting.[10,11]



Attempts to extend the 'cobalt-Hunsdiecker' sequence to alkylcarbonylcobalts, even to the t-butyl-substituted analogue (**20**), under the same conditions as described for the arylmethylcarbonylcobalt salophens (**7**)–(**9**), met with failure. Thus irradiation of compound (**20**) in the presence of either TEMPO or diphenyl disulphide led to only products (**21a**) and (**21b**), respectively. By contrast, and perhaps not unexpectedly, the allylcarbonylcobalt salophen (**22**) reacted with both TEMPO and diphenyl disulphide to produce 1:1 mixtures of the positional isomers (**23**) and (**24**) of the substituted decarbonylated products.

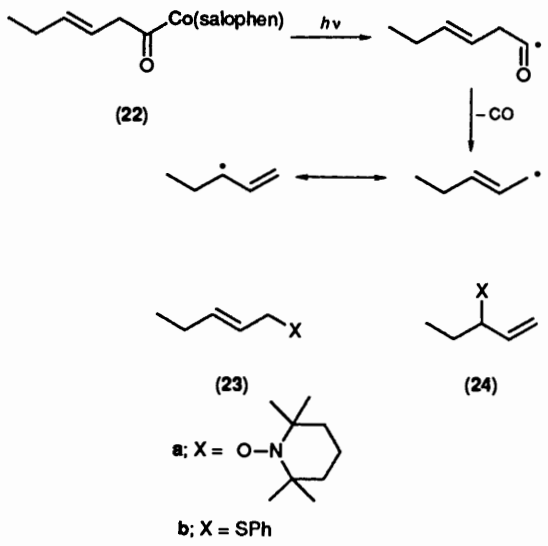
A similar pattern of reactivity to that observed above was found when studies were made of the homolysis–decarboxylation and radical trapping, following irradiation of a series of oxy-substituted acylcobalt salens[12] in the presence of radical-trapping agents. Thus, whereas irradiation of the arylmethyl (**25**) and the allyl (**26**) oxy-substituted carbonylcobalt salens in the presence of TEMPO produced the corresponding hydroxylamines (**14**) and (**27**), respectively, the related alkyl oxy-substituted salens (**28**), (**29**), and (**30**) led to only the mixed anhydrides (**31a**), (**31b**), and (**31c**), respectively. Interestingly, irradiation of compound (**29**) in the absence of a radical-trapping agent led to the butenolide (**32**) in good yield,[2] but attempts to extend this observation to the more challenging β-lactone system (**33**) were not successful.

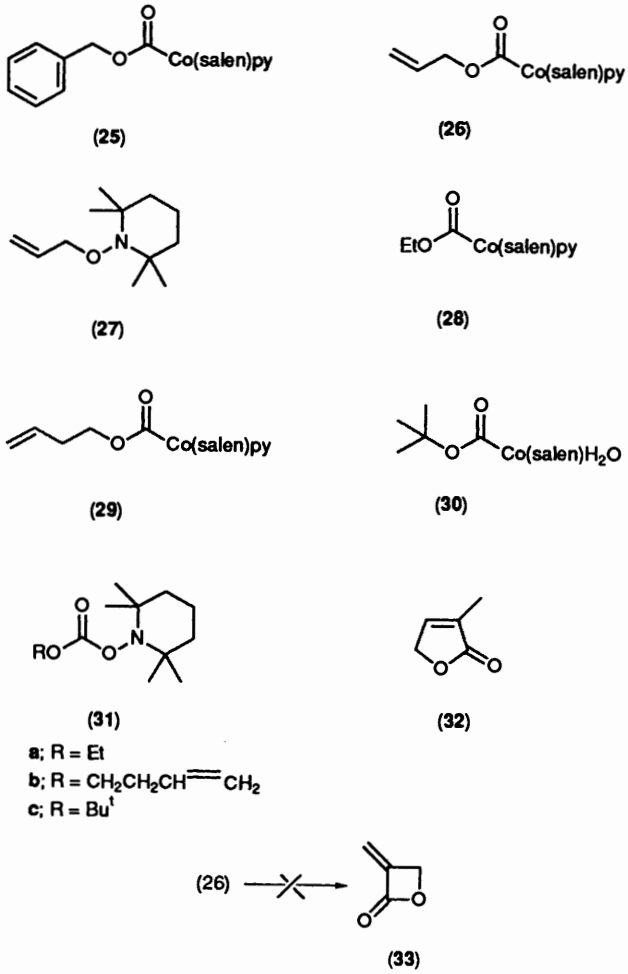
Experimental

For general experimental details see ref. 13.

Carboxylic Acid Chlorides.—Several acid chlorides were commercially available. 2,6-Dichlorophenylacetyl chloride[14] was produced from the corresponding carboxylic acid on treatment with thionyl chloride, whereas 1*H*-indole-3-acetyl chloride[15] was obtained after reaction of indole-3-acetic acid with phosphorus pentachloride.

† Irradiation of propanoylcobalt salophen in the presence of nitrogen monoxide instead leads to the corresponding *C*-nitrosocarbonyl product, which can be isolated as the oxazine adduct with 2,3-dimethylbuta-1,3-diene (G. W. Kirby and J. W. M. Mackinnon, *J. Chem. Soc., Perkin Trans. 1*, 1985, 887; G. W. Kirby, H. McGuigan, J. W. M. Mackinnon, D. McLean, and R. P. Sharma, *ibid.*, p. 1437).





Arylmethylcarbonylcobalt Salophen Complexes.—The acylcobalt salophens were prepared from the corresponding acid chlorides and sodium cobalt(I) salophen (**1**) according to the general procedure described in the preceding paper.[2]

Phenylacetylcobalt(III) *Salophen Complex* (**7a**).—By the general procedure, phenylacetyl chloride was treated with sodium cobalt(I) salophen(I) to give the acyl complex (**7a**) (42%), which was recrystallised from hexane–dichloromethane (1:1) as a bronze, crystalline solid, m.p. 163–165 °C (decomp.); ν_{max}($CHCl_3$) 2 920m, 1 730w, 1 610s, 1 580s, 1 450s, 1 140s, and 950w cm^{-1}; δ_H 7.85 (2 × CH=N), 7.5–7.3 (m, 8 × ArH), 7.1–7.05 (m, 5 × ArH), 6.9 (m, 2 × ArH), 6.6 (dd, J ~ 8.6 Hz, 2 × ArH), and 3.7 (CH_2CO); δ_C(100.62 MHz) 244.1 (C=O), 168.0, 144.0, 135.5, and 119.8 (C); 155.3, 134.8, 134.5, 129.1, 128.0, 127.1, 126.1, 123.6, 115.7, and 114.9 (CH); and 52.6 (CH_2) [m/z (FAB) M^+, 492. $C_{28}H_{21}CoN_2O_3$ requires M, 492].

p-*Methoxyphenylacetylcobalt*(III) *Salophen Complex* (**7b**).—By the general procedure, *p*-methoxyphenylacetyl chloride was treated with sodium cobalt(I) salophen (**1**) to give the acyl complex (**7b**) (25%), which was recrystallised from hexane–dichloromethane (1:5) as a bronze, crystalline solid, m.p. 157–160 °C (decomp.); ν_{max}($CHCl_3$) 2 940m, 1 710s, 1 603s, 1 440s, 1 305s, 1 140s, 1 130s, 960w, 910s, and 660m cm^{-1}; δ_H 7.7 (2 × CH=N), 7.4–6.5 (m, 16 × ArH), 4.9 (CH_2CO), and 3.7 (OMe); [m/z (FAB) (*p*-$MeOC_6H_4CH_2CO)^+$, 149 and (*p*-$MeOC_6H_4CH_2)^+$, 121. $C_9H_9O_2$ requires m/z, 149].

(2,6-*Dichlorophenyl*)*acetylcobalt*(III) *Pyridinato Salophen Complex* (**7c**).—By the general procedure, 2,6-dichlorophenylacetyl chloride was treated with sodium cobalt(I) salophen (**1**) to give the acyl complex (**7c**) (60%) as a dark red, crystalline solid, m.p. 189–191 °C; ν_{max}($CHCl_3$) 3 000w, 1 710w, 1 615s, 1 580m, 1 430m, 1 335w, and 1 160w cm^{-1}; δ_H(400 MHz) 8.6 (br s, 2 × pyH), 8.5 (2 × CH=N), 7.8 (m, 2 × ArH), 7.7 (t, J 7 Hz, 2 × pyH), 7.4 (d, J 8.5 Hz, 2 × ArH), 7.4–7.2 (m, 2 × pyH and 8 × ArH), 7.0 (app. d, J 8 Hz, 2 × ArH), 7.0 (dd, J 11.8 and 10.0 Hz, ArH), 6.7 (dt, J 1.0 and 8.0 Hz, 2 × ArH), and 5.4 (CH_2CO); δ_C(100.6 MHz) 242.8 (C=O), 168.7, 143.9, 135.5, and 119.9 (C); 154.9, 149.7, 136.0, 134.8, 134.5, 127.6, 127.5, 127.0, 124.4, 123.9, 115.1, and 114.9 (CH); and 60.4 (CH_2) {m/z (FAB) (Co[salophen]H)$^+$, 374 and (2,6-$Cl_2C_6H_3CH_2)^+$, 160. $C_7H_5Cl_2$ requires m/z, 160.9}.

1-H-*Indole*-3-*acetylcobalt*(III) *Pyridinato Salophen Complex* (**8**).—By the general procedure, 1*H*-indole-3-acetyl chloride was treated with sodium cobalt(I) salophen (**1**) to give the acyl complex (**8**) (43%) as an unstable, dark red solid. The crude product was used directly in the subsequent reactions.

Thiophene-2-*acetylcobalt*(III) *Pyridinato Salophen Complex* (**9**).—By the general procedure, thiophen-2-ylacetyl chloride was treated with the sodium cobalt(I) salophen (**1**) to give the acyl complex (**9**) (70%) as a dark red solid, m.p. 152–156 °C (decomp.); ν_{max}($CHCl_3$) 2 940w, 1 710m, 1 605s, 1 580s, 1 435m, 1 150m, and 920s cm^{-1}; δ_H(400 MHz) 8.7 (br s, 2 × pyH), 8.4 (2 × CH=N), 7.8 (dd, J 3.4 and 6.2 Hz, 2 × ArH), 7.6 (t, J 7.8 Hz, pyH), 7.4–7.2 (m, 2 × pyH and 8 × ArH), 7.0 (dd, J 1.2 and 5.1 Hz, thiophene=CH), 6.7 (dd, J 3.6 and 5.1 Hz, thiophene=CH), 6.6 (dt, J 1.4 and 7.9 Hz, 2 × ArH), 6.5 (d, J 3.6 thiophene=CH), and 5.1 (CH_2CO); {m/z (FAB) (Co[salophen]H)$^+$, 374 and (thiophene-2-acetyl)$^+$, 125. C_6H_5SO requires m/z, 125}.

Photolysis of Arylmethylcarbonylcobalt Salophen Complexes in the Presence of Radical-trapping Agents. General Procedure.—A solution of the acylcobalt(III) complex (1.00 mmol) and the radical-trapping agent (1.5–2.0 mmol) in dry, deoxygenated dichloromethane (60–80 ml) was irradiated at reflux under nitrogen, with a 300 W sunlamp (*d* 15–20 cm), until all the starting complex was consumed (monitored by TLC: silica; 1:10 MeOH–$CHCl_3$). In those cases where the acylcobalt complex used contained no pyridine ligand (*i.e.* where the cobalt existed as a five-co-ordinated species), then pyridine (2–3 mmol) was

added to the reaction mixture prior to irradiation. The solvent was evaporated off *in vacuo*, and then the brown solid was preadsorbed onto silica and subjected to gradient elution column chromatography (silica; light petroleum ⟶ 1:1 diethyl ether–light petroleum).

[(*Phenylthio*)*methyl*]*benzene* (**10a**).—By the general procedure a solution of the acyl complex (**7a**) (173.5 mg, 0.304 mmol) in dichloromethane (60 ml) was irradiated in the presence of diphenyl disulphide (132.5 mg, 0.608 mmol) and pyridine (24 mg, 0.034 mmol) for 52 h to give the title sulphide (**10a**) (153 mg, 48%) as low melting, white crystals, m.p. 36–38 °C (from MeOH) (lit.,[16] 39.5–40.5 °C).

1-*Methoxy*-4-[(*phenylthio*)*methyl*]*benzene* (**10b**).—By the general procedure, a solution of the acyl complex (**7b**) (510 mg, 0.977 mmol), diphenyl disulphide (213 mg, 1.96 mmol), and pyridine (231 mg, 2.93 mmol) in dichloromethane (85 ml) was irradiated for 42 h to give the title sulphide (**10b**) (126 mg, 56%) as a white, crystalline solid, m.p. 84.5–85.5 °C (from light petroleum); $\nu_{max}(CHCl_3)$ 1 610s cm^{-1}; δ_H 7.3 (m, 7 × ArH), 6.8 (d, *J* 8.8 Hz, 2 × ArH), 4.1 ($ArCH_2$), and 3.8 (OMe) [Found: C, 73.1; H, 6.2; S, 14.2%; M^+, 230.0754. Calc. for $C_{14}H_{14}SO$: C, 73.0; H, 6.1; S, 13.8%; *M*, 230.0765], consistent with the literature data.[17]

1,3-*Dichloro*-2-[(*phenylthio*)*methyl*]*benzene* (**10c**).—By the general procedure, a solution of the acyl complex (**7c**) (640 mg, 1.00 mmol) in dichloromethane (80 ml) was photolysed in the presence of diphenyl disulphide (327 mg, 1.50 mmol) for 50 h to give the *sulphide* (**10c**) (170 mg, 63%) as a pale yellow oil, ν_{max}(film) 3 090w and 1 585m cm^{-1}; δ_H 7.5–7.0 (m, 8 × ArH) and 4.4 ($ArCH_2$) (Found: C, 58.1; H, 3.9; Cl, 26.7%; M^+, 267.9864; $C_{13}H_{10}Cl_2S$ requires C, 58.0; H, 3.7; Cl, 26.4%; *M*, 267.9880).

3-[(*Phenylthio*)*methyl*]-1H-*indole* (**11a**).—By the general procedure, a solution of the acyl complex (**8**) (404 mg, 0.61 mmol), diphenyl disulphide (249 mg, 1.14 mmol), and pyridine (79 mg, 1.00 mmol) in dichloromethane (150 ml) was irradiated for 6.75 h to give: (i) 3-methyl-1*H*-indole (eluted first) (9 mg, 7%) as a dark oil, $\nu_{max}(CHCl_3)$ 3 480s cm^{-1}; δ_H 7.9 (br s, NH), 7.6–6.9 (m, 5 × ArH), and 2.3 (d, *J* 1.2 Hz, Me), which were consistent with the literature data,[18] and (ii) the sulphide (**11a**) (eluted second) (115.5 mg, 48%) as a white, fluorescent solid, m.p. 80.5–81.5 °C (from light petroleum); $\nu_{max}(CHCl_3)$ 3 480s, 1 620w, and 1 585m cm^{-1}; δ_H 7.9 (br s, NH), 7.7 (m, ArH), 7.4–7.0 (m, 9 × ArH), and 4.3 (d, *J* 0.8 Hz, $ArCH_2$) (Found: C, 75.2; H, 5.5; N, 5.6%; M^+, 239.0743. Calc. for $C_{15}H_{13}NS$: C, 75.3; H, 5.4; N, 5.8%; *M* 239.0769), which were consistent with the literature data.[19]

2-[*Phenythio*)*methyl*]*thiophene* (**11b**).—By the general procedure, a solution of the acyl complex (**9**) (577 mg, 1.00 mmol) and diphenyl disulphide (327 mg, 1.50 mmol) was irradiated for 23 h to give the *title sulphide* (**11b**) (138 mg, 79%) as a yellow oil; ν_{max}(film) 2 920m and 1 585m cm^{-1}; δ_H 7.5–7.1 (m, Ph and thiophene H), 6.9 (app d, *J* 3.7 Hz, 2 × thiophene H), and 4.3 (d, *J* 3.1 Hz, CH_2S); δ_C(20.15 MHz) 128.9 and 124.9 (C); 130.4, 128.9, 126.75, and 126.2 (CH); and 33.8 (CH_2) (Found: M^+, 206.0195. $C_{11}H_{10}S_2$ requires *M*, 206.0225).

[(*Phenylseleno*)*methyl*]*benzene* (**12**).—By the general procedure, a solution of the acyl complex (**7a**) (498 mg, 1.00 mmol) and diphenyl diselenide (624 mg, 2.00 mmol) was photolysed for 20.5 h to give the *title selenide* (**12**) (145 mg, 57%) as a pale yellow oil, ν_{max}(film) 3 095m, 1 580m, 745s, and 740s cm^{-1}; δ_H 7.5–7.1 (m, 6 × ArH), 7.0–6.8 (m, 2 × ArH), and 4.3 (CH_2Se); δ_C(62.9 MHz) 141.7 and 124.6 (C); 133.6, 128.9, 127.4, 126.6, and 126.1 (CH); and 35.6 (CH_2) (Found: M^+, 253.9680. $C_{11}H_{10}SSe$ requires *M*, 253.9669).

2,6-*Dichlorobenzyl Bromide* (**13a**).—By the general procedure, a solution of the acylcobalt complex (**7c**) (320 mg, 0.5 mol) and bromotrichloromethane (198 mg, 1.00 mmol) in dichloromethane (60 ml) was irradiated for 16 h to give the bromide (**13a**) (39.8 mg, 33.3%) as a white, crystalline solid, m.p. 54–55 °C (from light petroleum) (lit.,[20] 55–57 °C).

2,6-*Dichlorobenzyl Alcohol* (**13b**).—A solution of the acyl complex (**7c**) (480 mg, 0.75 mmol) in dichloromethane (90 ml) was irradiated under aerobic conditions for 20 h, and then the solvent was evaporated off *in vacuo*. The residue was dissolved in methanol (60 ml) and the solution was then treated with aq. alkaline sodium borohydride (2 × 142 mg, 7.47 mmol), at room temperature for 26 h, as described by the general procedure[13] to furnish the alcohol (**13b**) (61 mg, 46%) as a white, crystalline solid, m.p. 96.5–98.5 °C (from light petroleum–diethyl ether) (lit.,[18] 96–98 °C).

N-*Benzyloxy*-2,2,6,6-*tetramethylpiperidine* (**14**).—By the general procedure, a solution of the acyl complex (**7a**) (285.5 mg, 0.50 mmol), pyridine (35 mg, 0.50 mmol), and TEMPO (117 mg, 0.75 mmol) in dichloromethane (80 ml) was irradiated for 14 h to give the *adduct* (**14**) (76 mg, 61%) as a pale yellow oil; ν_{max}(film) 2 980s and 1 610w cm^{-1}; δ_H 7.3 (br s, Ph), 4.8 ($ArCH_2$), 1.5 (br s, 3 × ring CH_2), and 1.2 (m, 4 × Me) (Found: M^+, 247.1938. $C_{16}H_{25}NO$ requires *M*, 247.1936).

2,6-*Dichlorobenzaldehyde* (**19**).—A solution of the acylcobalt complex (**7c**) (649 mg, 1.00 mmol) and triethylamine (101 mg, 1.00 mmol) in dimethylformamide (80 ml) was irradiated for 28 h in the presence of nitrogen monoxide, as described by the general procedure,[5] to give the aldehyde (126.5 mg, 72%) as white needles, m.p. 69–70 °C (from light petroleum) (lit.,[18] 71 °C).

1,2-*Bis*-(2,6-*dichlorophenyl*)*ethane* (**18**).—A solution of the acyl complex (**7c**) (480 mg, 0.75 mmol) in de-aerated dichloromethane (80 ml) was irradiated under nitrogen for 26 h at reflux. The solvent was evaporated off *in vacuo* and the solid residue was then purified by chromatography (silica; 1:1 diethyl ether–light petroleum) to give the dimer (**18**) (47 mg, 40%), which was recrystallised from light petroleum as a white, crystalline solid, m.p. 155–157 °C (lit.,[6] 156–157 °C) (Found: C, 52.7; H, 3.1%; M^+, 317.9535. Calc. for $C_{14}H_{10}Cl_4$: C, 52.5; H, 3.1%; *M*, 317.9537).

2,2-*Dimethylpropanoylcobalt*(III) *Salophen Complex* (**20**).—By the general procedure, 2,2-dimethylpropanoyl chloride was treated with sodium cobalt(I) salophen (**1**) to give the acyl complex (77%) as a maroon, powdery solid, m.p. 161–166 °C (decomp.); $\nu_{max}(CHCl_3)$ 2 930m, 1 725s, 1 610s, 1 585s, 1 440m, 1 380m, 1 140m, and 960w cm^{-1}; δ_H(400 MHz) 8.6 (2 × CH=N), 7.9 (br, 2 × ArH), 7.4–7.3 (m, 8 × ArH), 6.7 (br s, 2 × ArH), and 1.0 (3 × Me) [*m/z* (FAB) 537. $C_{30}H_{28}CoN_3O_3$ requires *M*, 537].

2,2,6,6-*Tetramethylpiperidinyl* 2,2-*Dimethylpropanoate* (**21a**).—According to the general procedure, a solution of 2,2-dimethypropanoylcobalt(III) salophen (**20**) (458 mg, 1 mmol) and TEMPO (1.1 mmol) in dichloromethane (200 ml) was irradiated for 15 h to give the title ester (**21a**) (113 mg, 47%) as a yellow oil; ν_{max}(film) 2 990 and 1 760 cm^{-1}; δ_H 1.6 (br s, ring $[CH_2]_3$), 1.3 (s, Bu^t), and 1.2 and 1.0 (2 × s, 4 × Me) [Found: *m/z*, 226.1813. $C_{13}H_{24}NO_2$ ($M^+ - CH_3$) requires *m/z*, 226.1807].

S-*Phenyl* 2,2-*Dimethylpropanethiolate* (**21b**).—According to the general procedure, a solution of 2,2-dimethylpropanoylcobalt(III) salophen (**20**) (537 mg, 1.2 mmol) and diphenyl disulphide (327 mg, 1.5 mmol) in dichloromethane (80 ml) was irradiated for 24 h to give the *title thioester* (**21b**) (61 mg, 27%) as a pale yellow oil; ν_{max}(film) 1 690 cm^{-1}; δ_H 7.4 (br s, Ph) and 1.3 (s, Bu^t) (Found: M^+, 194.0737. $C_{11}H_{14}SO$ requires *M*, 194.0765).

Hex-3-*enoylcobalt*(III) *Pyridinato Salophen* (**22**).*—According to the general procedure, hex-3-enoyl chloride (4.75 mmol) was treated with sodium cobalt(I) salophen (**1**) (5 mmol) to give the acylcobalt complex (**22**) (1.90 g, 73%) as a maroon, powdery solid, m.p. > 300 °C; ν_{max}($CHCl_3$) 2 960, 1 720, 1 610, 1 580, and 930 cm^{-1}; δ_H 8.7 (br, 2 × pyH), 8.6 (2 × CH=N), 7.9 (m, 2 × ArH), 7.7 (m, pyH), 7.4 (m, 8 × ArH and 2 × pyH), 6.7 (m, 2 × ArH), 5.3 (m, 2 × CH=), 4.3 (d, *J* 6.1 Hz, CH_2CO), 1.7 (m, MeCH_2), and 0.8 (t, *J* 7.4 Hz, Me); *m/z* (FAB) 471 (M^+ + 1 − py).

2,2,6,6-*Tetramethyl*-N-*pent*-2-*enyloxypiperidine* (**23a**) *and* N-(1-*Ethylprop*-2-*enyloxy*)-2,2,6,6-*tetramethylpiperidine* (**24a**).—According to the general procedure, a solution of hex-3-enoylcobalt(III) pyridinato salophen (**22**) (257 mg, 0.47 mmol) and TEMPO (1.3 mol equiv.) in dichloromethane (100 ml) was irradiated for 40 h to give a 1:1 mixture of isomers of compounds (**23a**) and (**24a**) (50 mg, 47%) as a pale yellow oil; ν_{max}(film) 2 940 and 1 640 cm^{-1}; δ_H 6.0–5.3 (m, C*H*=CH_2 and CH=CH), 5.1–4.9 (m, =CH_2), 4.4–3.9 (m, OCH and OCH_2), and 2.3–0.7 (m, Et, ring $[CH_2]_3$, and 4 × Me) (Found: *m/z*, 156.1382 and 69.0704. $C_9H_{18}NO$ and C_5H_9 require *m/z*, 156.1388 and 69.0704, respectively).

Pent-2-*enyl Phenyl Sulphide* (**23b**) *and* 1-*Ethylprop*-2-*enyl Phenyl Sulphide* (**24b**).*—According to the general procedure, a solution of hex-3-enoylcobalt(III) pyridinato salophen (**22**) (490 mg, 0.9 mmol) and diphenyl disulphide (436 mg, 2 mmol) in dichloromethane (200 ml) was irradiated for 38 h to give a 1:1 mixture of isomers of compounds (**23b**) and (**24b**) (70 mg, 44%) as an oil; ν_{max}(film) 1 650 and 1 590 cm^{-1}; δ_H 7.5–7.1 (m, Ph), 5.6–5.4 (m, C*H*=CH_2 and CH=CH), 5.0–4.7 (m, =CH_2) 3.6–3.4 (m, PhSCH_2 and PhS*CH*), 2.2–1.5 (m, CH_2Me), 1.0 (t, *J* 7 Hz, =CHCH$_2$*Me*), and 1.0 (t, *J* 7 Hz, =CHOCH$_2$*Me*).

Sodium Cobalt(I) *Salen* (**1**).[12]—Mercury (0.9 ml) was added to sodium (0.24 g, 10.4 mmol; freshly cut into small lumps) under nitrogen, and the reaction flask was then swirled vigorously until an exothermic reaction was observed (in those cases where there was no immediate sign of reaction, the flask was gently warmed with a bunsen flame). Addition of further mercury (0.9 ml) with gentle swirling gave 1% sodium amalgam, which was allowed to cool to room temperature. The amalgam was added to a suspension of cobalt(II) salen (2.5 mmol) in dry, deoxygenated tetrahydrofuran (THF) (100 ml) at room temperature, and the mixture was then stirred under nitrogen in the dark for 2–3 h to give a turquoise solution of sodium cobalt(I) salen (**1**). The solution was transferred *via* cannulation under nitrogen into a clean, dry flask, where it was used immediately.

Preparation of Oxycarbonylcobalt(III) *Pyridinato Salen Complexes: General Procedure.*—The chloroformate (2.5 mmol) was added neat, under nitrogen, to a stirred solution of sodium cobalt(I) salen (**1**) (2.5 mmol) in dry, deoxygenated THF (100 ml) at −78 °C. The turquoise colour of cobalt(I) salen was discharged and was replaced by a red-brown suspension. The mixture was stirred in the dark and allowed to warm to room temperature during 30 min and was then evaporated *in vacuo* (dark; < 30 °C) to leave a solid residue. The residue was dissolved in 5% pyridine–dichloromethane (*ca.* 30 ml) and purified by column chromatography on alumina woelm, with 5% pyridine in dichloromethane as eluant. The product was eluted as an orange-red solution, which was diluted with hexane and evaporated *in vacuo* (dark; < 30 °C). Further additions of dichloromethane (~30 ml) and hexane (~100 ml) were necessary in order to facilitate azeotropic distillation of excess of pyridine to leave the oxycarbonylcobalt complex as a crystalline orange solid.

Benzyloxycarbonylcobalt(III) *Pyridinato Salen* (**25**).—According to the general procedure, benzyl chloroformate (3.6 ml, 2.5 mmol) reacted with sodium cobalt(I) salen (**1**) (2.5 mmol) at −78 °C to give the cobalt complex (**25**) (750 mg, 57%) as an orange, crystalline solid, m.p. > 230 °C; ν_{max}($CHCl_3$) 2 920, 1 660, 1 620, 1 600, and 905 cm^{-1}; δ_H 8.6–8.5 (m, 2 × PyH), 7.8 (2 × CH=N), 7.4–6.9 (m, 13 × ArH and 3 × pyH), 6.6–6.4 (m, 2 × ArH), 5.3 (PhCH_2), and 3.5 (N$[CH_2]_2$); *m/z* (FAB) 461 (M^+ + 1 − py).

Allyloxycarbonylcobalt(III) *Pyridinato Salen* (**26**).—According to the general procedure, allyl chloroformate (265 ml, 2.5 mmol) reacted with sodium cobalt(I) salen (**1**) (2.5 mmol) at −78 °C to give the cobalt complex (**26**) (760 mg, 62%) as an orange-yellow, crystalline solid, m.p. > 260 °C; ν_{max}($CHCl_3$) 2 920, 1 660, 1 620, 1 600, 1 040, and 905 cm^{-1}; δ_H($CDCl_3$) 8.5 (m, 2 × pyH), 7.8 (2 × CH=N), 7.7–7.6 (m, 1 × pyH), 7.4–7.0 (m, 8 × ArH), 6.6–6.4 (m, 2 × ArH), 5.7–5.3 (m, C*H*=CH_2), 4.7–5.0 (m, =CH_2 and OCH_2), and 3.6 (N$[CH_2]_2$N); *m/z* (FAB) 411 (M^+ + 1 − py).

Ethoxycarbonylcobalt(III) *Pyridinato Salen* (**28**).—According to the general procedure, ethyl chloroformate (239 ml, 2.5 mmol) reacted with sodium cobalt(I) salen (**1**) (2.5 mmol) at −78 °C to give the *alkoxycarbonylcobalt complex* (**28**) (1.10 g, 92%) as an orange, crystalline solid, m.p. > 230 °C; ν_{max}($CHCl_3$) 2 925, 1 650, 1 620, 1 600, 1 060, and 905 cm^{-1}; δ_H 8.6–8.5 (m, 2 × pyH), 7.8 (2 × CH=N), 7.7–7.6 (m, 1 × pyH), 7.4–7.0 (m, 6 × ArH and 2 × pyH), 6.6–6.4 (m, 2 × ArH), 4.2 (q, *J* 7 Hz, OCH_2Me), 3.5 (N $[CH_2]_2$N), and 0.8 (t, *J* 7 Hz, Me); *m/z* (FAB) 398 (M^+ − py) (Found: C, 59.8; H, 5.1; N, 8.8. $C_{24}H_{24}CoN_3O_4$ requires C, 60.4; H, 5.1; N, 8.8%).

But-3-*enyloxycarbonylcobalt*(III) *Pyridinato Salen* (**29**).—According to the general procedure, but-3-enyl chloroformate (225 mg, 1.67 mmol) reacted with sodium cobalt(I) salen (**1**) (1.67 mmol) at −78 °C to give the cobalt complex (**29**) (310 mg, 37%) as a red-orange, powdery solid, m.p. > 275 °C; ν_{max}($CHCl_3$) 1 675, 1 615, 1 600, 1 060, and 905 cm^{-1}; δ_H 8.6–8.5 (m, 2 × pyH), 7.8 (2 × CH=N), 7.7–7.6 (m, 1 × pyH), 7.4–7.0 (m, 6 × ArH and 2 × pyH), 6.6–6.4 (m, 2 × ArH), 5.7–5.2 (m, CH=CH_2), 4.9–4.8 (m, =CH_2), 4.2 (t, *J* 6.5 Hz, OCH_2), 3.7 (N$[CH_2]_2$N), and 1.9 (m, OCH_2CH_2); *m/z* (FAB) 424 (M^+ − py).

t-Butoxycarbonylcobalt(III) *Aqua Salen* (**30**).—Di-t-butyl dicarbonate (574 ml, 2.5 mmol) was added neat, under nitrogen, to a stirred solution of sodium cobalt(I) salen (**1**) (25 mmol) in dry, deoxygenated THF (100 ml) at −78 °C. The turquoise colour of cobalt(I) salen was discharged and was replaced by a red-brown suspension, when the mixture was stirred in the dark and allowed to warm to room temperature during 30 min. The mixture was then poured into water (100 ml) and partially evaporated *in vacuo* to give the cobalt complex (**30**) (520 mg,

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47%) as a brown precipitate, which was collected by suction filtration and dried under high vacuum, m.p. > 230 °C; $\nu_{max}(CHCl_3)$ 2 920, 1 680, 1 605, 1 060, and 905 cm^{-1}; *m/z* (FAB) 427 ($M^+ + 1 - H_2O$).

Photolysis of an Alkyloxycarbonylcobalt(III) *Pyridinato Salen Complex in the Presence of TEMPO. General Procedure.*—A solution of the cobalt complex (0.1–0.5 mmol) and TEMPO (1 mol equiv.) in dry, deoxygenated dichloromethane (50–100 ml) was irradiated using a 300 W sunlamp (*d* 10–20 cm) under reflux in nitrogen for 5–18 h. The progress of the reaction was monitored by TLC (silica; 5:95 MeOH–CH_2Cl_2) and interrupted when all the starting material had disappeared. The solvent was evaporated off *in vacuo*, and the residue was then purified by column chromatography (silica; 1:1 light petroleum–diethyl ether).

N-*Benzyloxy*-2,2,6,6-*tetramethylpiperidine* (**14**).—According to the general procedure, a solution of benzyloxycarbonylcobalt(III) pyridinato salen (**25**) (350 mg, 0.65 mmol) and TEMPO (1 equiv.) in dichloromethane (150 ml) was irradiated for 11 h to give the adduct (141 mg, 88%) as an oil, which showed identical spectroscopic data with those described earlier.

N-*Allyloxy*-2,2,6,6-*tetramethylpiperidine* (**27**).—According to the general procedure, a solution of allyloxycarbonylcobalt(III) pyridinato salen (**26**) (210 mg, 0.43 mmol) and TEMPO (1 mol equiv.) in dichloromethane (100 ml) was irradiated for 4 h to give the *adduct* (**27**) (66 mg, 78%) as an oil; ν_{max}(film) 2 940, 1 640, and 935 cm^{-1}; δ_H 6.1–5.7 (m, $CH{=}CH_2$), 5.4–5.0 (m, $=CH_2$), 4.3–4.2 (m, OCH_2), 1.5 (br s, ring $[CH_2]_3$), and 1.1 (br s, 4 × Me) (Found: *m/z*, 196.1759. $C_{12}H_{22}NO$ ($M^+ - H$) requires *m/z*, 196.1701).

Ethyl 2,2,6,6-*Tetramethylpiperidin*-1-*yl Carbonate* (**31a**).—According to the general procedure, a solution of ethoxycarbonylcobalt(III) pyridinato salen (**28**) (199 mg, 0.42 mmol) and TEMPO (1 mol equiv.) in dichloromethane (100 ml), was irradiated for 18 h to give the title carbonate (**31a**) (75 mg, 78%) as an oil; ν_{max}(film) 2 940, 1 770, 790, and 735 cm^{-1}; δ_H 4.2 (q, *J* 7 Hz, OCH_2), 1.6 (br s, ring $[CH_2]_3$), 1.3 (t, *J* 7 Hz, CH_2Me), and 1.2 and 1.1 (2 × s, 4 × Me) (Found: *m/z*, 214.1446. $C_{11}H_{20}NO_3$ ($M^+ - CH_3$) requires *m/z*, 214.1443).

But-3-*enyl* 2,2,6,6-*Tetramethylpiperidin*-1-*yl Carbonate* (**31b**).—According to the general procedure, a solution of but-3-enyloxycarbonylcobalt(III) pyridinato salen (80 mg, 0.16 mmol) and TEMPO (1 mol equiv.) in dichloromethane (30 ml) was irradiated for 5 h to yield the *title carbonate* (**31b**) (10 mg, 25%) as a liquid; ν_{max}(film) 2 940, 1 770, 1 220, and 915 cm^{-1}; δ_H 6.0–5.5 (m, $CH{=}CH_2$), 5.2–4.9 (m, $=CH_2$), 4.1 (t, *J* 6.7 Hz, OCH_2), 2.4 (m, OCH_2CH_2), 1.5 (br s, ring $[CH_2]_3$), and 1.1 and 1.0 (2 × s, 4 × Me) (Found: M^+, 255.1864. $C_{14}H_{25}NO_3$ requires *M*, 255.1844).

t-Butyl 2,2,6,6-*Tetramethylpiperidin*-1-*yl Carbonate* (**31c**).—According to the general procedure, a solution of t-butoxycarbonylcobalt(III) aqua salen (**30**) (200 mg, 0.45 mmol) and TEMPO (1 mol equiv.) in dichloromethane (100 ml) was irradiated for 18 h to give the title carbonate (**31c**) (20 mg, 18%) as a liquid; ν_{max}(film) 2 940, 1 760, 1 160, and 680 cm^{-1}; δ_H 1.6 (br s, ring $[CH_2]_3$), 1.5 (s, Bu^t), and 1.2 and 1.1 (2 × s, 4 × Me); *m/z* (FAB) 281 ($M^+ + 1 + Na$).

2-*Methylbut*-2-*enolide* (**32**).[21]—A solution of but-3-enyloxycarbonylcobalt(III) pyridinato salen (**29**) (200 mg, 0.39 mmol) in dry, deoxygenated dichloromethane (100 ml) was irradiated under reflux for 48 h under nitrogen. The solvent was evaporated off *in vacuo*, and the residue was then purified by column chromatography (silica; 50:50 light petroleum–diethyl ether) to give the lactone (**32**) (24 mg, 62%) as a yellow oil;[21] ν_{max}(film) 2 940, 1 750, 1 655, 940, and 840 cm^{-1}; δ_H 7.2 (m, =CH), 4.8 (m, OCH_2), and 1.9 (m, Me) (Found: M^+, 98.0377. Calc. for $C_5H_6O_2$: *M*, 98.0368).

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