Acylcobalt Salophen Reagents. Precursors to Acyl Radical Intermediates for Use in Carbon-to-Carbon Bond-forming Reactions to Alkenes

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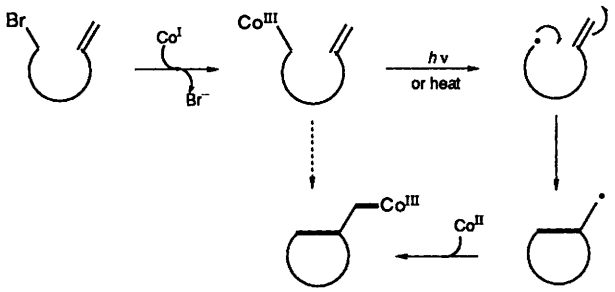
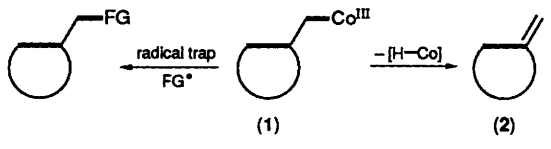
Acylcobalt salophen reagents (**6**) are conveniently synthesised from carboxylic acid chlorides following treatment with the sodium derivative (**5**) produced from reduction of cobalt(II) salophen with sodium amalgam in tetrahydrofuran at room temperature. The acylcobalt salophens (**6**) undergo homolytic cleavage in the presence of light from a conventional 300 W sunlamp to give acyl radicals (**24**) which then undergo additions to activated carbon-to-carbon double bonds, leading to enones, *viz.* (**26**) [following dehydrocobaltation from presumed organocobalt intermediates (**25**)], or saturated ketones, *viz.* (**34**) [following H-quenching of intermediates (**25**)]. Intramolecular cyclisations of the acylcobalt salophens (**42a**) and (**42b**) lead to the ylidenecyclopentanones (**43**) and (**45**), respectively.

In earlier work we have described the use of a range of cobalt(I)-mediated intramolecular radical cyclisation reactions involving alkyl and aryl halides, leading to cobalt-functionalised carbo- and hetero-cyclic molecules (sometimes referred to as 'cobalt-group transfer') (Scheme 1).[1] In other studies we have synthesized a number of alkylcobalt(III) complexes, similar to (**1**), and shown that on thermal or photolytic homolysis in the presence of radical-trapping agents they provide useful routes to both carbon- and heteroatom- (*e.g.*, O, N, S, Se, halogen) bond-forming products (Scheme 2)[2]; in the absence of radical-trapping agents the same alkylcobalt complexes (**1**) readily undergo β-elimination (dehydrocobaltation), producing alkenes, *i.e.* compounds (**2**).[3] We now describe the synthesis of a variety of acylcobalt salophens, and an examination of their effectiveness as precursors to acyl radicals for use in carbon-to-carbon bond-forming reactions to alkenes.[4]



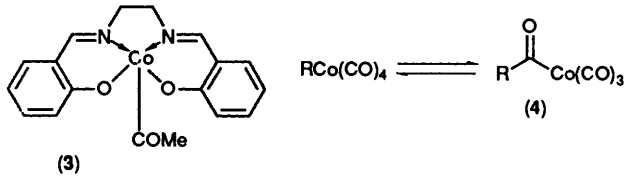
Scheme 1. 'Cobalt-group Transfer'.



FG = O,N,S,Se,halogen,carbon

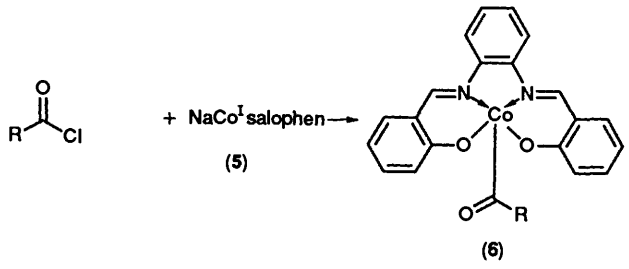
Scheme 2.

Acyl radicals were first described as long ago as 1949, when they were produced by treatment of certain terpene aldehydes with peroxides.[5] At the outset of our studies, apart from useful extensions of this early method,[6] no other general method existed for the formation of acyl radicals. In contemporary studies, however, other researchers have now highlighted the uses of phenylseleno esters[7] and *S*-acyl xanthates[8] as suitable precursors to acyl radicals. The first and only description of an acylcobalt compound was that of the simple acetylcobalt salen (**3**), prepared from sodium cobalt(I) salen and acetyl chloride by Costa and Mestroni.[9] Scheffold and Orlinski,[10] however, have described the vitamin B_{12}-catalysed nucleophilic acylation of carbon-to-carbon double bonds from an anhydride, which probably proceeds *via* a transient acylcobalt similar to compound (**3**), and the chemistry of some *in situ* generated acylcobalt tricarbonyls, *viz.* (**4**), has also been described.[11]



We have found that acylcobalt 'salophen' reagents can be synthesized conveniently, and in high yields, from carboxylic acid chlorides following treatment with the sodium derivative (**5**)[1] produced from reduction of cobalt(II) salophen with 1% sodium amalgam in tetrahydrofuran (THF) at room temperature. In this manner, we have prepared a wide range of primary, secondary, tertiary, allyl, vinyl, aryl, arylmethyl, alkoxy, and amino acylcobalt salophens (**6**), all of which are brightly coloured, stable crystalline materials. In some preparations we have also found it convenient to use the carboxylic acid mixed anhydrides with 2,6-dichlorobenzoic acid, in place of carboxylic acid chlorides, and in other preparations we have used sodium cobalt(I) salen [1] instead of compound (**5**) to prepare acylcobalt salens; *cf.* (**3**). Perhaps somewhat surprisingly we were unable to produce stable benzoylcobalt complexes from benzoyl chloride or from its *o*- and *p*-nitro derivatives, using these methods.

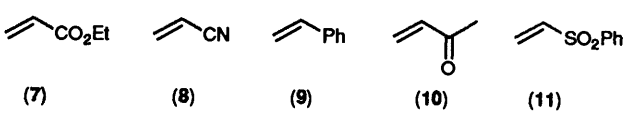
To investigate the potential for the acylcobalt salophens in transferring an acyl moiety to carbon-to-carbon double bonds, the compounds (**6**) were homolysed, using light from an ordinary 300 W sunlamp in the presence of a range of olefinic substrates. Like their alkyl relatives,[1,3] the acyl radicals generated in this way were nucleophilic in character and only reacted with those double bonds which were: (a) substituted by



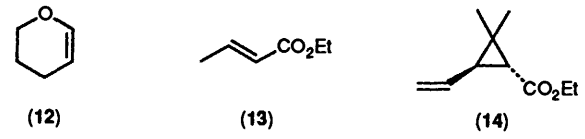
a; R = Et ; b; R = ; c; R = pentyl;

d; R = ; e; R = CH_2Bu^t ; f; R = OEt ;

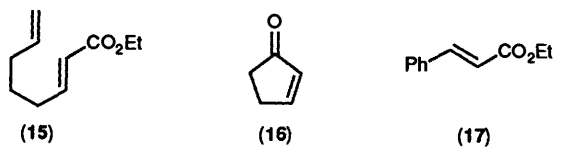
g; R = Me_2N ; h; R =



(7) (8) (9) (10) (11)



(12) (13) (14)

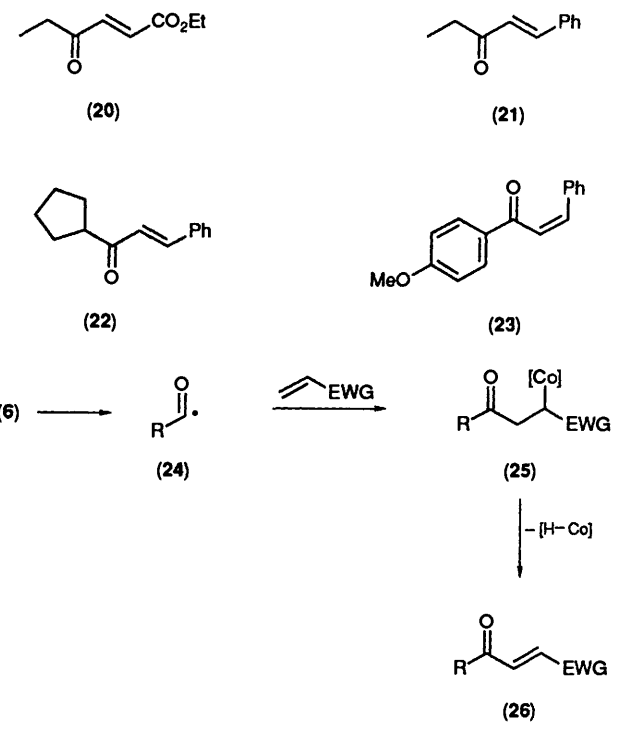


(15) (16) (17)

(18) (19)

electron-withdrawing groups, and (b) lacking substitution at the carbon centre β to the electron-withdrawing group. For example, whereas the olefinic substrates (7)–(11) all reacted with the acylcobalt salophens (6), leading to products of addition, the related alkenes (12)–(19) were recovered unchanged.

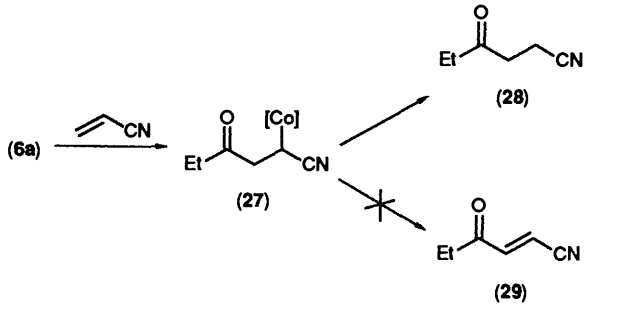
Thus, irradiation of a de-aerated, refluxing solution of propanoylcobalt salophen (6a) and ethyl propenoate (7) in dichloromethane produced the known *E*-isomer (20) of ethyl 4-oxohex-2-enoate contaminated with traces of the corresponding *Z*-isomer. The salophen (6a) also reacted with styrene (9) leading to the enone (21) as a 2:1 mixture of *Z* and *E* isomers. In a similar manner, irradiation of the cyclopentylcarbonyl (6b) and 4-methoxybenzoylcobalt salophen (6d) in the presence of styrene (9) led to the corresponding enones (22) and (23), respectively. In all of these reactions the acylcobalt salophen reagent is behaving as a source of the corresponding acyl radical intermediate (24) which adds in a Michael fashion to the olefinic substrate, leading to a short-lived organocobalt



(20) (21) (22) (23) (24) (25) (26)

EWG = electron-withdrawing group

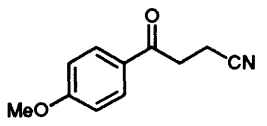
Scheme 3.



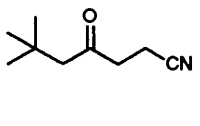
(27) (28) (29)

species, *viz.* (25); β-elimination (dehydrocobaltation) from species (25) then leads to the conjugated enone products (26) (see Scheme 3).[3] The acylcobalt reagents therefore assume a dual role, *viz.* nucleophilic acyl reagents with a capacity for the cobalt moiety to effect an oxidation (*i.e.*, elimination of H–Co).

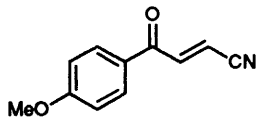
It was interesting and surprising to observe that when the propanoylcobalt salophen (6a) was treated with acrylonitrile (8) in place of ethyl propenoate (7) and styrene (9), the major product was the saturated nitrile (28), *i.e.* the product of hydrogen-atom quenching of the presumed organocobalt intermediate (27) rather than the product (29) resulting from competitive β-elimination. The same pattern of reactivity was also observed during reactions between acrylonitrile (8) and other acylcobalts. Thus, both cobalt salophens (6d) and (6e) reacted with acrylonitrile to produce compounds (30) and (31), respectively; in both instances, however, smaller amounts of the corresponding products resulting from competitive dehydrocobaltation, *i.e.* (32) and (33), were produced concurrently. Likewise, when methyl vinyl ketone (10) was used as the alkene substrate, mixtures of saturated (34) and unsaturated (35) products were produced from reactions with



(30)



(31)



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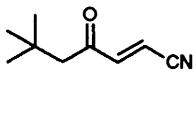
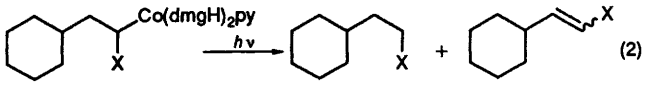


(33)

the acylcobalt salophen reagents (**6b**), (**6c**), (**6d**), and (**6e**) [equation (1)].

The origin of the dichotomous reactivity observed in the carbon-to-carbon bond-forming reactions between acylcobalt salophens (**6**) and alkenes containing CO_2Et and Ph substitution (leading to alkene products) and those containing CN and COMe substitution (leading to alkane products) is not immediately obvious. In contemporaneous work with the *alkyl*cobaloximes (**36a**) and (**36b**) carrying α-CO_2Et and α-CN substituents, Giese *et al.*[12] have made similar observations, *i.e.* the amount of alkane product (**37**) increases with respect to that of alkene product (**38**) with increasing electron-withdrawing capacity of the α-substituent (*viz.* CN > CO_2Et). The same authors also observed that the amount of alkane product from both complexes (**36a**) and (**36b**) could be increased by changing to a protic solvent [equation (2)]. These data indicated that the formation of alkanes in these reactions occurs *via* an ionic cleavage of the carbon-to-cobalt bond, which competes under favourable conditions with the more familiar dehydrocobaltation (β-elimination) pathway leading to alkene formation.

It is probable that a similar rationale can be used to explain our own results with the *acyl*cobalt salophens (**6**).[13] In this context, it was interesting to observe that when the cobalt salophen (**6e**) was irradiated with either acrylonitrile (**8**) or methyl vinyl ketone (**10**) in the presence of fully deuteriated acetic acid *only* alkane products were observed, containing 35 and 20% deuterium incorporation, respectively. The same reactions in the absence of acetic acid produced approximately equal amounts of alkanes (**31**)/(**34e**) together with the



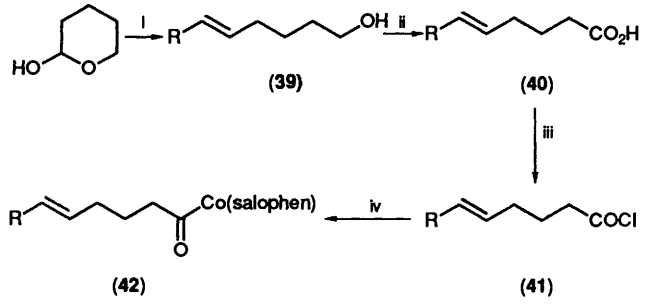
(36) (37) (38) (2)

a; X = CN ; **b** ; X = CO_2Et

	Solvent		
(36a)	CH_2Cl_2	23	77
(36a)	$MeCO_2H$	88	12
(36b)	CH_2Cl_2	0	100
(36b)	$MeCO_2H$	58	42

corresponding alkenes, *i.e.* (**33**) and (**35e**), respectively (see earlier discussion).

To augment the use of acyl radical intermediates for carrying out oxidative additions of the type shown above we also examined corresponding intramolecular cyclisations from the acylcobalt salophen reagents (**42a**) and (**42b**).[14] Each of these compounds was easily synthesized as outlined in Scheme 4.

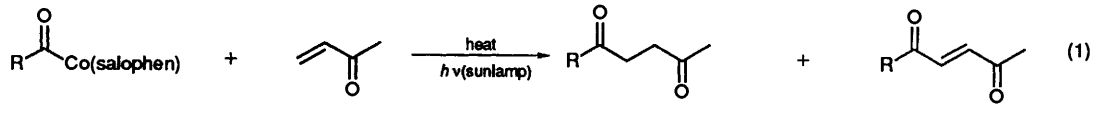


(39) (40) (41) (42)

a; R = Ph ; **b** ; R = CO_2Et

Scheme 4. *Reagents:* i, $R\bar{C}H\overset{+}{P}Ph_3$; ii, Jones; iii, $SOCl_2$; iv, Co^I-(salophen).

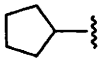
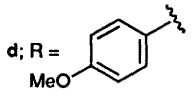
Irradiation of complex (**42a**) in dichloromethane for 20 h followed by chromatography and crystallisation led to the crystalline *Z*- and the oily *E*-isomer of the benzylidenecyclopentanone (**43**) in a combined yield of 42%. Similarly the acylcobalt reagent (**42b**) underwent intramolecular cyclisation leading to a 1:1 mixture of the saturated (**44**) and the unsaturated ketoester (**45**).

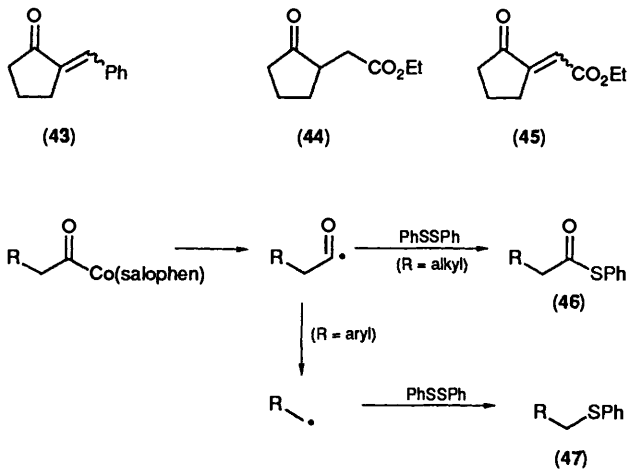


(1)

(34) (35)

(6b)	97(33%)	3(1%)
(6c)	63(12%)	37(7%)
(6d)	46(20%)	54(23%)
(6e)	64(21%)	36(12%)

b; R =  ; **c**; R = pentyl ; **d**; R =  ; **e**; R = CH_2Bu^t ;



As a corollary we also examined the reactions between the acylcobalt salophen compounds (**6**) and diphenyl disulphide and diphenyl diselenide. With simple alkylcobalt salophens, the corresponding phenylthio and phenylseleno esters (**46**) were produced in high yields (70–80%). Homolyses of those cobalt salophen reagents derived from arylmethylacetyl chlorides, however, in the presence of diphenyl disulphide instead produced only arylmethyl sulphides (**47**) resulting from *in situ* decarbonylation. This latter reaction, which amounts to a variation of the familiar Hunsdiecker reaction, is amplified and discussed in more detail in the accompanying paper.[15]

Experimental

For general experimental details see ref. 1.

Sodium Cobalt(I) *Salophen* (**5**).—Mercury (1.4 ml) was added to sodium (0.36 g, 16 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 (1.3 ml) with gentle swirling gave 1% sodium amalgam, which was allowed to cool to room temperature. The amalgam was added to a solution of cobalt(II) salophen (1.86 g, 5 mmol)[1] in dry, deoxygenated THF (200 ml) at room temperature, and the mixture was then stirred under nitrogen in the dark for 2 h to give a dark green solution of sodium cobalt(I) salophen (**5**). The solution was transferred *via* cannulation under nitrogen into a clean, dry flask, where it was used immediately.

Preparation of Acylcobalt(III) *Salophen Complexes. General Procedure.*—The carboxylic acid chloride (4.5–5.1 mmol) was added neat under nitrogen to a stirred solution of sodium cobalt(I) salophen (**5**) (5.0 mmol) in dry, deoxygenated THF (200 ml) at room temperature. The green colour of cobalt(I) salophen was discharged and was replaced by a dark red solution. The solution was stirred at 25 °C in the dark for 1–2 h 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 a dark 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 allow azeotropic distillation of excess of pyridine to leave the acylcobalt complex as a powdery, maroon solid. Microanalytical data proved erratic and unreliable.

Propanoylcobalt(III) *Salophen Complex* (**6a**).—According to the general procedure, propanoyl chloride (434 μl, 5.0 mmol) was treated with sodium cobalt(I) salophen (**5**) (5.0 mmol) to give the acylcobalt complex (**6a**) (1.97 g, 82%), which was recrystallised from dichloromethane–hexane as dark red crystals, m.p. 196–200 °C (decomp.); $\nu_{max}(CHCl_3)$ 2 950, 1 760, 1 700, 1 610, and 1 580 cm^{-1}; δ_H 8.5 (2 × CH=N), 8.0–6.6 (m, 12 × ArH), 3.5 (q, *J* 7.2 Hz, CH_2CO), and 0.9 (t, *J* 7.2 Hz, Me); *m/z* (FAB) 431 ($M^+ + 1$).

Cyclopentylcarbonylcobalt(III) *Salophen Complex* (**6b**)—According to the general procedure, cyclopentanecarboxylic acid chloride (742 mg, 5.0 mmol) was treated with sodium cobalt(I) salophen (**5**) (5.0 mmol) to give the acylcobalt complex (**6b**) (1.82 g, 74%), which was recrystallised from 2% pyridine in hexane–dichloromethane (1:2) as dark red crystals, m.p. 217–221 °C (decomp.); $\nu_{max}(CHCl_3)$ 2 950, 1 730, and 1 600 cm^{-1}; δ_H 8.5 (2 × CH=N) 7.9–7.6 (m, 2 × ArH), 7.4–7.1 (m, 8 × ArH), 6.7–6.5 (m, 2 × ArH), 4.7 (m, CHCO), and 1.8–1.4 (m, 4 × ring CH_2); $\delta_C(CDCl_3)$ 250.1 (C=O), 168.1, 155.6, 144.3, 134.7, 134.0, 127.1, 123.6, 119.8, 116.1, 114.9, 58.8, 31.4, and 25.3; *m/z* (FAB) 471 ($M^+ + 1$).

Hexanoylcobalt(III) *Salophen Complex* (**6c**)—According to the general procedure, hexanoyl chloride (1.50 ml, 10 mmol) was treated with sodium cobalt(I) salophen (**5**) (10 mmol) in THF (400 ml) to give the acylcobalt complex (**6c**) (4.13 g, 87%) as a maroon, powdery solid, m.p. 158–160 °C; $\nu_{max}(CHCl_3)$ 2 930, 1 725, 1 610, and 1 585 cm^{-1}; δ_H 8.6 (2 × CH=N), 7.8 (m, 2 × ArH), 7.4–7.2 (m, 8 × ArH), 6.7 (m, 2 × ArH), 3.5 (t, *J* 7.1 Hz, $COCH_2$), 1.4–0.9 (m, 3 × CH_2), and 0.6 (t, *J* 7.2 Hz, Me); *m/z* (FAB) 473 ($M^+ + 1$).

p-*Methoxybenzoylcobalt*(III) *Pyridinato Salophen Complex* (**6d**).—According to the general procedure, *p*-methoxybenzoyl chloride (5.0 mmol) was treated with sodium cobalt(I) salophen (**5**) (5.0 mmol) to give the acylcobalt complex (**6d**) (1.64 g, 56%) as a maroon solid; $\nu_{max}(CHCl_3)$ 2 950, 1 660, 1 610, and 1 580 cm^{-1}; δ_H 9.2 (br s, 2 × pyH), 8.6 (2 × CH=N), 8.2 (d, *J* 9.1 Hz, 2 × ArH), 8.0–7.9 (m, 2 × ArH), 7.7–7.2 (m, 3 × pyH and 8 × ArH), 6.7 (d, *J* 9.1 Hz, 2 × ArH), 6.6 (m, 2 × ArH), and 3.8 (OMe); δ_C 235.9 (C=O), 168.3, 162.6, 155.9, 150.0, 144.0, 136.9, 134.6, 127.1, 124.3, 124.1, 119.2, 114.7, 114.6, and 46.2; *m/z* (FAB) 587 (M^+).

3,3-*Dimethylbutanoylcobalt*(III) *Salophen Complex* (**6e**)—According to the general procedure, 3,3-dimethylbutanoyl chloride (1.32 ml, 9.5 mmol) was treated with sodium cobalt(I) salophen (**5**) (10 mmol) in THF (400 ml) to give the acylcobalt complex (**6e**) (3.16 g, 70%) as a dark red, powdery solid, m.p. 157–173 °C; $\nu_{max}(CHCl_3)$ 2 950, 1 730, and 1 610 cm^{-1}; δ_H 8.6 (m, 2 × CH=N), 7.8 (m, 2 × ArH), 7.4–7.2 (m, 8 × ArH), 6.7 (m, 2 × ArH), 3.4 ($COCH_2$), and 0.7 (3 × Me); *m/z* (FAB) 473 ($M^+ + 1$).

Ethoxycarbonylcobalt(III) *Salophen Complex* (**6f**).—According to the general procedure, ethyl chloroformate was treated with sodium cobalt(I) salophen (**5**) to give the acylcobalt complex (**6f**) (1.17 g, 49.5%) as a dark red, crystalline solid, m.p. 181–185 °C; $\nu_{max}(CHCl_3)$ 2 960w, 1 690m, 1 615s, 1 580s, 1 430m, 1 380m, 1 340m, 1 155m, and 1 075s cm^{-1}; δ_H(400 MHz) 8.8 (2 × CH=N), 8.0 (m, 2 × ArH), 7.5–7.4 (m, 8 × ArH), 6.8 (dt, *J* 1.0 and 6.8 Hz, 2 × ArH), 4.1 (q, *J* 7.1 Hz, OCH_2), and 0.6 (t, *J* 7.1 Hz, Me); δ_C(100.6 MHz) 168.0, 160.0, 144.3, and 120.0 (C); 156.3, 135.0, 134.0, 127.1, 124.3, 116.5, and 114.8 (CH); 66.3 (CH_2); and 14.2 (CH_3); *m/z* (FAB) (Co[salophen]H)$^+$, 374; (EtOCO)$^+$, 73.

Dimethylcarbamoylcobalt(III) *Pyridinato Salophen Complex* (**6g**).—According to the general procedure, dimethylcarbamoyl chloride was treated with sodium cobalt(I) salophen (**5**) to give the acylcobalt complex (**6g**) (2.09 g, 79.3%), which was recrystallised from 2% pyridine in hexane–dichloromethane (1:2) as dark red needles, m.p. 221–222 °C; $\nu_{max}(CHCl_3)$ 2 920m, 1 730w, 1 610s, 1 580s, 1 140s, 1 080m, 950w, and 860w cm^{-1}; δ_H 8.8 (br s, 2 × pyH), 8.4 (2 × CH=N), 7.8–7.7 (m, 2 × ArH), 7.6–7.5 (m, pyH), 7.3–7.1 (m, 2 × pyH and 8 × ArH), 6.7–6.5 (m, 2 × ArH), and 3.2 (br, Me_2N); δ_C (100.6 MHz) 171.5, 168.2, 144.5, 120.2, 155.0, 149.8, 136.2, 134.5, 134.4, 127.0, 124.0, 123.2, 115.0, and 38.7br w (Found: *m/z* $(M - py)^+$, 445. $C_{23}H_{20}CoN_3O_3$ requires *m/z*, 445).

Cyclopent-2-enylacetylcobalt(III) *Pyridinato Salophen Complex* (**6h**).—According to the general procedure, cyclopent-2-enylacetyl chloride (5 mmol) was treated with sodium cobalt(I) salophen (**5**) (5 mmol) to give the acylcobalt complex (**6h**) (1.52 g, 54%) as a dark brown solid, m.p. 161–166 °C (decomp.); $\nu_{max}(CHCl_3)$ 2 940, 1 730, 1 610, 1 580, 1 445, and 920 cm^{-1}; δ_H 8.7 (br s, 2 × pyH), 8.5 (2 × CH=N), 7.8 (m, 2 × ArH), 7.6 (m, pyH), 7.4–7.3 (m, 2 × pyH and 8 × ArH), 6.6 (m, 2 × ArH), 5.5 (m, CH=C), 5.3 (m, =CH), 3.7 (dd, *J* 17.6 and 8.2 Hz, C*H*HCO), 3.6 (1 H, dd, *J* 17.6 and 5.7 Hz, CH*H*CO), 3.0 (m, =CCH), 2.0 (m, CH_2C=), 1.7 (m, ring C*H*H), and 1.0 (m, ring CH*H*); *m/z* (FAB) 483 $(M^+ + 1 - py)$.

Photolysis of Acylcobalt(III) *Salophen Complexes in the Presence of Deactivated Alkenes. General Procedure.*—A solution of the acylcobalt complex (1.0 mmol) and freshly distilled alkene (5 mmol) in dry, deoxygenated dichloromethane (120–200 ml) was irradiated under reflux, using a 300 W sunlamp (*d* 10–20 cm) for 24–72 h, under nitrogen. The progress of the reaction was monitored by TLC (silica; 98:2 CH_2Cl_2–EtOH) 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; light petroleum–diethyl ether).

(E)-*Ethyl* 4-*Oxohex*-2-*enoate* (**20**).—According to the general procedure, a solution of propanoylcobalt(III) salophen (**6a**) (430 mg, 1 mmol) and ethyl acrylate (**7**) (2.16 ml, 20 mmol) in dichloromethane (150 ml) was irradiated for 43 h to give the (*E*)-enone (**20**) (55 mg, 35%) as a sweet smelling, pale yellow oil; $\nu_{max}(CHCl_3)$ 2 920, 1 720, and 1 645 cm^{-1}; δ_H 7.1 (d, *J* 16 Hz, COCH=), 6.6 (d, *J* 16 Hz, =C*H*CO_2Et), 4.3 (q, *J* 7 Hz, CH_2O), 2.7 (q, *J* 7 Hz, CH_2CO), 1.3 (t, *J* 7 Hz, Me), and 1.1 (t, *J* 7 Hz, Me) (Found: M^+, 156.0760. Calc. for $C_8H_{12}O_3$: 156.0786).[16]

(E)- *and* (Z)-1-*Phenylpent*-1-*en*-3-*one* (**21**).—According to the general procedure, a solution of propanoylcobalt(III) salophen (**6a**) (430 mg, 1.0 mmol) and styrene (**9**) (1.15 ml, 10 mmol) in dichloromethane (200 ml) was irradiated for 44 h to give: (i) the (Z)-*enone* (**21**) (42 mg, 26%) (eluted first) as a sweet-smelling, yellow oil; ν_{max}(film) 1 685, 1 605, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 7.6–7.3 (m, 5 × ArH), 6.8 (d, *J* 12.9 Hz, PhC*H*=), 6.2 (d, *J* 12.9 Hz, =CHCO), 2.5 (q, *J* 7.2 Hz, CH_2), and 1.1 (t, *J* 7.2 Hz, Me) (Found: M^+, 160.0893. $C_{11}H_{12}O$ requires *M*, 160.0887) and (ii) the (*E*)-enone (**21**) (18 mg, 12%) (eluted second), which was recrystallised as a pale yellow solid, m.p. 38–40 °C (from hexane) (lit.,[17] 40 °C); $\nu_{max}(CHCl_3)$ 1 665, 1 605, and 975 cm^{-1}; δ_H 7.8–7.3 (m, 5 × ArH and PhC*H*=), 6.7 (d, *J* 16.2 Hz, =CHCO), 2.7 (q, *J* 7.4 Hz, CH_2), and 1.1 (t, *J* 7.4 Hz, Me) (Found: M^+, 160.0886).

(E)- *and* (Z)-1-*Cyclopentyl*-3-*phenylprop*-2-*en*-1-*one* (**22**).—According to the general procedure, a solution of cyclopentylcarbonylcobalt(III) salophen (**6b**) (942 mg, 2.0 mmol) and styrene (**9**) (2.3 ml, 20 mmol) in dichloromethane (300 ml) was irradiated for 38 h to give: (i) the (Z)-*enone* (**22**) (51 mg, 13%) (eluted first) as a yellow oil; ν_{max}(film) 1 690, 1 610, and 765 cm^{-1}; $\delta_H(CHCl_3)$ 7.6–7.3 (m, 5 × ArH), 6.8 (d, *J* 12.8 Hz, PhC*H*=), 6.2 (d, *J* 12.8 Hz, =CHCO), 3.3–2.7 (m, COC*H*$[CH_2]_2$), and 1.9–1.2 (m, 4 × ring CH_2) (Found: M^+, 200.1180. $C_{14}H_{16}O$ requires *M*, 200.1200), and (ii) the (*E*)-enone[18] (**22**) (51 mg, 13%) (eluted second) as a yellow oil; ν_{max}(film) 1 665, 1 610, and 980 cm^{-1}; δ_H 7.8–6.9 (m, 5 × ArH and PhC*H*=), 6.8 (d, *J* 16.2 Hz, =CHCO), 3.4–3.1 (m, COC*H*$[CH_2]_2$), and 2.0–1.2 (m, 4 × ring CH_2) (Found: M^+, 200.1180).

(Z)-1-(4-*Methoxyphenyl*)-3-*phenylprop*-2-*en*-1-*one* (**23**).—According to the general procedure, a solution of *p*-methoxybenzoylcobalt(III) pyridinato salophen (**6d**) (587 mg, 1.0 mmol) and styrene (**9**) (1.15 ml, 10 mmol) in dichloromethane (200 ml) was irradiated for 45 h to give the (*Z*)-enone[19] (**23**) (28 mg, 12%) as a yellow oil; $\nu_{max}(CHCl_3)$ 1 650, 1 595, and 1 570 cm^{-1}; δ_H 7.9 (d, *J* 9.0 Hz, 2 × ArH), 7.4–7.2 (m, 5 × ArH), 6.9 (d, *J* 12.9 Hz, PhC*H*=), 6.9 (d, *J* 9.0 Hz, 2 × ArH), 6.5 (d, *J* 12.9 Hz, =CHCO), and 3.8 (OMe) (Found: M^+, 238.0998. Calc. for $C_{16}H_{14}O_2$: *M*, 238.0993).

4-*Oxohexanenitrile* (**28**)—According to the general procedure, a solution of propanoylcobalt(III) salophen (**6a**) (430 mg, 1 mmol) and acrylonitrile (**8**) (0.99 ml, 15 mmol) in dichloromethane (200 ml) was irradiated for 40 h to give the nitrile[20] (**28**) (58 mg, 52%) as a yellow oil; ν_{max}(film) 2 250, 1 715, and 1 120 cm^{-1}; δ_H 2.9–2.3 (m, $CH_2CO[CH_2]_2$) and 1.1 (t, *J* 7.4 Hz, Me); δ_C 206.6 (C=O), 126.0 (C≡N), 37.3, 35.7, 11.4, and 7.6 (Found: M^+, 111.0684. Calc. for C_6H_9NO: 111.0683). ^1H NMR data [6.9 (d, *J* 16.4 Hz, COCH=) and 6.1 (d, *J* 16.4 Hz, =CHCN)] indicated that the nitrile contained a small amount (< 5%) of the corresponding (*E*)-enone (**29**).

4-(4-*Methoxyphenyl*)-4-*oxobutanenitrile* (**30**) *and* 4-(4-*Methoxyphenyl*)-4-*oxobut*-2-*enenitrile* (**32**).—According to the general procedure, a solution of *p*-methoxybenzoylcobalt(III) pyridinato salophen (**6d**) (587 mg, 1 mmol) and acrylonitrile (**8**) (0.99 ml, 15 mmol) in dichloromethane (200 ml) was irradiated for 45 h to give: (i) the (E)-*enone* (**32**) (20 mg, 11%) (eluted first), which was recrystallised as a white solid, m.p. 59–61 °C (from diethyl ether–hexane); $\nu_{max}(CHCl_3)$ 2 240, 1 665, and 1 600 cm^{-1}; δ_H 8.0 (d, *J* 9 Hz, 2 × ArH), 7.8 (d, *J* 16 Hz, COCH=), 7.0 (d, *J* 9 Hz, ArH), 6.5 (d, *J* 16 Hz, =CHCN), and 3.9 (OMe) (Found: M^+, 187.0638. $C_{11}H_9NO_2$ requires *M*, 187.0633) and (ii) the *nitrile* (**30**) (30 mg, 16%) (eluted second), which was recrystallised as a white solid, m.p. 204–206 °C (from MeOH); $\nu_{max}(CHCl_3)$ 2 260, 1 675, and 1 600 cm^{-1}; δ_H 7.9 (d, *J* 9 Hz, 2 × ArH), 6.9 (d, *J* 9 Hz, 2 × ArH), 3.9 (OMe), 3.3 (t, *J* 7.4 Hz, $COCH_2$), and 2.7 (t, *J* 7.4 Hz, CH_2CN) (Found: M^+, 189.0796. $C_{11}H_{11}NO_2$ requires *M*, 189.0788).

6,6-*Dimethyl*-4-*oxoheptanenitrile* (**31**) *and* (E)-6,6-*Dimethyl*-4-*oxohept*-2-*enenitrile* (**33**).—According to the general procedure, a solution of 3,3-dimethylbutanoylcobalt(III) salophen (**6e**) (472 mg, 1 mmol) and acrylonitrile 0.99 ml, 15 mmol) in dichloromethane (200 ml) was irradiated for 40 h to give: (i) the (E)-*enone* (**33**) (13 mg, 9%) (eluted first) as a yellow oil; ν_{max}(film) 2 970, 2 240, 1 695, and 1 610 cm^{-1}; δ_H 6.9 (d, *J* 16.2 Hz, =CHCO), 6.3 (d, *J* 16.2 Hz, =CHCN), 2.5 (CH_2), and 1.0 (Me_3) (Found: M^+, 151.0969. $C_9H_{13}NO$ requires *M*, 151.0996), and (ii) the nitrile (**31**) (23 mg, 15%) (eluted second) as a yellow oil; ν_{max}(film) 2 960, 2 255, and 1 715 cm^{-1}; δ_H 2.9–2.4 (m, $[CH_2]_2CO$), 2.3 (CH_2), and 1.0 (Me_3) (Found: *m/z*, 138.0982 $(M^+ - CH_3)$ requires *m/z*, 138.0982). ^1H NMR data [6.8 (d,

J 11.5 Hz, =CHCO) and 5.7 (d, *J* 11.5 Hz, CHCN)] indicated that the nitrile (**33**) contained a small amount (<5%) of the corresponding (*Z*)-enone.

1-*Cyclopentylpentane*-1,4-*dione* (**34b**).—According to the general procedure, a solution of cyclopentylcarbonylcobalt(III) salophen (**6b**) (942 mg, 2 mmol) and freshly distilled methyl vinyl ketone (**10**) (1.66 ml, 20 mmol) in dichloromethane (300 ml) was irradiated for 60 h to give the *dione* (**34b**) (110 mg, 33%) as a yellow oil; $\nu_{max}(CHCl_3)$ 1 710 cm^{-1}; δ_H 3.0 (m, $COCH[CH_2]_2$), 2.8 ($CO[CH_2]_2CO$), 2.1 (COMe), and 2.1–1.3 (m, 4 × ring CH_2) (Found: M^+, 168.1128. $C_{10}H_{16}O_2$ requires *M*, 168.1149). ^1H NMR data [6.9 (2 × =CH), 2.4 (COMe)] indicated that the 1,4-dione contained a small amount (<5%) of the corresponding (*E*)-enedione (**35b**).

Decane-2,5-*dione* (**34c**) *and* (E)- *and* (Z)-*Dec*-3-*ene*-2,5-*dione* (**35c**).—According to the general procedure, a solution of hexanoylcobalt(III) salophen (**6c**) (472 mg, 1 mmol) and freshly distilled methyl vinyl ketone (**10**) (0.83 ml, 10 mmol) in dichloromethane (200 ml) was irradiated for 40 h to give: (i) the (*E*)-enone (**35c**) (4 mg, 2%) (eluted first) as a yellow solid; (lit.,[21] m.p. 52–53 °C); $\nu_{max}(CHCl_3)$ 2 920, 1 680, and 1 620 cm^{-1}; δ_H 6.8 (s, CH=CH), 2.6 (t, *J* 7 Hz, CH_2CO), 2.4 (MeCO), 1.8–1.2 (m, $[CH_2]_3$), and 0.9 (t, *J* 7 Hz, Me) (Found: *m/z*, 139.0757. $C_8H_{11}O_2$ requires *m/z*, 139.0758); (ii) the dione[22] (**34c**) (21 mg, 12%) (eluted second) as a yellow oil; ν_{max}(film) 1 710 cm^{-1}; δ_H 2.7 ($CO[CH_2]_2CO$), 2.5 (t, *J* 7 Hz, $COCH_2$), 2.2 (COMe), and 1.8–0.8 (m, $[CH_2]_3Me$) (Found: M^+, 170.1295. Calc. for $C_{10}H_{18}O_2$: *M*, 170.1306), and (iii) the (*Z*)-enone corresponding to (**35c**) (9 mg, 5%) (eluted third) as a yellow oil; $\nu_{max}(CHCl_3)$ 2 920, 1 700, and 1 610 cm^{-1}; δ_H 6.3 (s, CH=CH), 2.5 (t, *J* 7 Hz, CH_2CO), 2.3 (Me), 1.8–1.1 (m, $[CH_2]_3$), and 0.9 (t, *J* 7 Hz, Me).

(E)-1-(4-*Methoxyphenyl*)*pent*-2-*ene*-1,4-*dione* (**35d**) *and* 1-(4-*Methoxyphenyl*)*pentane*-1,4-*dione* (**34d**).—According to the general procedure, a solution of *p*-methoxybenzoylcobalt(III) pyridinato salophen (**6d**) (587 mg, 1 mmol) and freshly distilled methyl vinyl ketone (**10**) (3.32 ml, 40 mmol) in dichloromethane (185 ml) was irradiated for 50 h to give: (i) the (*E*)-enone (**35d**) (eluted first) (12 mg, 6%) as a yellow, crystalline solid, m.p. 62–64 °C (from diethyl ether–light petroleum) (lit.,[23] 66 °C); $\nu_{max}(CHCl_3)$ 2 880, 1 660, and 1 610 cm^{-1}; δ_H 8.0 (d, *J* 9.0 Hz, 2 × ArH), 7.7 (d, *J* 15.7 Hz, COCH=), 7.1 (d, *J* 15.8 Hz, =CHCO), 7.0 (d, *J* 9.0 Hz, 2 × ArH), 3.9 (OMe), and 2.4 (COMe) (Found: M^+, 204.0777. Calc. for $C_{12}H_{12}O_3$: *M*, 204.0786), (ii) the dione (**34d**) (eluted second) (41 mg, 20%), which was recrystallised as a white, crystalline solid, m.p. 56–57 °C (from diethyl ether–light petroleum) (lit.,[24] 58–59 °C) (Found: C, 70.1; H, 7.0%; M^+, 206.0947. Calc. for $C_{12}H_{14}O_3$: C, 69.9; H, 7.1%; *M*, 206.0943), and (iii) the unstable (*Z*)-enone corresponding to (**35d**) (39 mg, 19%) as a yellow oil; δ_H 7.9 (d, *J* 8.9 Hz, 2 × ArH), 6.9 (d, *J* 8.9 Hz, 2 × ArH), 6.9 (d, *J* 12.1 Hz, COCH=), 6.5 (d, *J* 12.1 Hz, =CHCO), 3.9 (OMe), and 2.3 (COMe), which isomerised on purification by chromatography (silica; diethyl ether) to give the (*E*)-enone (**35d**) (39 mg) as a low melting, yellow solid (m.p. 62–64 °C), whose spectral data were identical with those obtained previously.

7,7-*Dimethyloctane*-2,5-*dione* (**34e**) *and* (E)- *and* (Z)-7,7-*Dimethyloct*-3-*ene*-2,5-*dione* (**35e**).—According to the general procedure, a solution of 3,3-dimethylbutanoylcobalt(III) salophen (**6e**) (472 mg, 1 mmol) and freshly distilled methyl vinyl ketone (**10**) (0.83 ml, 10 mmol) in dichloromethane (200 ml) was irradiated for 40 h to give: (i) the (E)-*enone* (**35e**) (8 mg, 5%) (eluted first) as a yellow oil; ν_{max}(film) 2 960, 1 682, and 1 622 cm^{-1}; δ_H 6.8 (CH=CH), 2.5 (CH_2), 2.4 (COMe), and 1.0 (3 × Me) (Found: M^+, 168.1146. $C_{10}H_{16}O_2$ requires *M*, 168.1150), (ii) the dione (**34e**)[25] (36 mg, 21%) (eluted second) as a yellow oil; ν_{max}(film) 2 950 and 1 710 cm^{-1}; δ_H 2.7 ($[CH_2]_2$), 2.3 (CH_2), 2.2 (COMe), and 1.0 (3 × Me) (Found: M^+, 170.1308. Calc. for $C_{10}H_{18}O_2$: *M*, 170.1306), and (iii) the (Z)-*enone* corresponding to (**35e**) (12 mg, 7%) (eluted third) as a yellow oil; ν_{max}(film) 2 956, 1 699, and 1 616 cm^{-1}; δ_H 6.2 (CH=CH), 2.4 (CH_2), 2.3 (COMe), and 1.0 (3 × Me) (Found: M^+, 168.1140).

6-*Phenylhex*-5-*en*-1-*ol* (**39a**).—A solution of sodium methoxide in methanol [Na (1.4 g) in MeOH (20 ml)] was added dropwise to a solution of 2-hydroxytetrahydropyran (3.06 g, 0.03 mol) and benzyltriphenylphosphonium bromide (13 g, 0.03 mol) in methanol (20 ml) at room temperature. After 16 h, the mixture was evaporated to a small volume and water (100 ml) was added. The aq. layer was acidified (2M-HCl) and extracted with dichloromethane (3 × 50 ml). The combined extracts were dried ($MgSO_4$), then evaporated *in vacuo* and the residue was purified by chromatography (silica; light petroleum–ethyl acetate 5:1, then 3:1) to give the title hexenol (**39a**) (3.72 g, 71%) as an oil and then as a mixture of *E*- and *Z*-isomers (*E*:*Z* 40:60 by ^1H NMR analysis), b.p. 130 °C at 0.4 mmHg (lit.,[26] b.p. 174–175 °C at 17 mmHg); ν_{max}(film) 3 350, 3 015, 2 940, 1 600, 1 500, 1 435, 1 075, and 705 cm^{-1}; δ_H 7.3 (br s, Ph), 7.5–7.0 (m, other CH), 5.6 (dt, *J* 12 and 7.5 Hz, $=CHCH_2$, *Z*-isomer), 2.6 (m, CH_2OH), 2.3 (m, $CH_2CH=$), and 1.6–1.5 (m, 2 × CH_2) (Found: M^+, 176.1194. Calc. for $C_{12}H_{16}O$: *M*, 176.1201).

6-*Phenylhex*-5-*enoic Acid* (**40a**).—The alcohol (**39a**) (2.36 g) was oxidised with Jones' reagent in acetone to yield the crude *acid* (**4a**) (1.1 g, 43%) which was used without further purification; ν_{max}(film) 1 710 cm^{-1}; δ_H 10.6 (br s, CO_2H), 7.2 (br s, Ph), 7.6–6.9 (m, other =CH), 5.6 (2 dt, *J* 12 and 7.5 Hz, $=CHCH_2$, *Z*-isomer), and 2.5–1.6 (m, 3 × CH_2) (Found: M^+, 190.0999. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

6-*Phenylhex*-5-*enoyl Chloride* (**41a**).—A solution of the acid (**40a**) (1.4 g) in dry diethyl ether (20 ml) was treated with thionyl chloride (3 ml, distilled) and the mixture was then stirred at room temperature for 5 h. Evaporation *in vacuo* and distillation at reduced pressure yielded the acid chloride (**41a**) (1.1 g, 86%), b.p. 101–103 °C at 0.2 mmHg; ν_{max} 1 810 cm^{-1}, which was used immediately.

Ethyl 7-*Hydroxyhept*-2-*enoate* (**39b**).—A solution of 2-hydroxytetrahydropyran (3.06 g, 0.03 mol) and (ethoxycarbonylmethylene)triphenylphosphorane (11.5 g, 0.034 mol) in acetonitrile (50 ml) was heated under reflux for 48 h. The solution was evaporated *in vacuo* and the residue was then chromatographed (silica; 1:1 light petroleum–diethyl ether) to give *ethyl* 7-*hydroxyhept*-2-*enoate* (**39b**) (3.6 g, 70%) as an oil and then as a mixture of E- and Z-*isomers* (*E*:*Z* 77:23 by ^1H NMR analysis); ν_{max}(film) 3 400, 2 960, 1 715, 1 655, 1 375, 870, and 760 cm^{-1}; δ_H 7.0 (dt, *J* 18 and 7 Hz, $CH_2CH=$, *E*-isomer), 6.2 (dt, *J* 12 and 7 Hz, $CH_2CH=$, *Z*-isomer), 5.9–5.7 (m, $EtO_2CCH=$), 4.2 (q, *J* 7 Hz, OCH_2Me), 3.6 (m, CH_2OH), 2.2 (m, $CH_2CH=$), 1.6 (m, 2 × CH_2), and 1.3 (t, *J* 7 Hz, OCH_2Me) (Found: M^+, 172.1111. $C_9H_{16}O_3$ requires *M*, 172.1100).

1-*Ethyl Hydrogen Hept*-2-*enedioate* (**40b**).—The alcohol (**39b**) (3 g) in acetone (20 ml) was oxidised with Jones' reagent to yield the crude acid ester (**40b**) (1.47 g, 45%); ν_{max}(film) 3 500–3 000 and 1 710 cm^{-1}; δ_H 9.8 (br s, CO_2H), 6.9 (dt, *J* 17 and 7.5 Hz, $CH_2CH=$, *E*-isomer), 6.3–5.7 (m, other CH=), 4.2 (q, *J* 7.1 Hz, OCH_2Me), 2.5–1.6 (6 H, m, 3 × CH_2), and 1.3 (t,

J 7.1 Hz, OCH_2Me) (Found: *m/z*, 168.0779; $C_9H_{14}O_4 - H_2O$ requires *m/z*, 168.0.0786).

Ethyl 6-Chlorocarbonylhex-2-enoate (**41b**).—A solution of the acid (**40b**) (1.8 g) in dry diethyl ether (10 ml) was treated with thionyl chloride (3 ml, distilled) and the mixture was stirred at room temperature for 5 h. Evaporation *in vacuo* and distillation at reduced pressure yielded the ester acid chloride (**41b**) (1.38 g, 68%), b.p. 167–169 °C at 1 mmHg; ν_{max}(film) 1 800 and 1 720 cm^{-1}, which was used immediately.

(E)-6-*Phenylhex-5-enoylcobalt*(III) *Salophen Complex* (**42a**).—According to the general procedure, 6-phenylhex-5-enoyl chloride (**41a**) (1.05, g, 5 mmol) was treated with sodium cobalt(I) salophen (**5**) (5 mmol) to give the title acylcobalt complex (**24a**) (2.4 g, 76%) as a maroon solid; $\nu_{max}(CHCl_3)$ 1 720 cm^{-1}; δ_H 8.4 (2 × CH=N), 7.7 (m, 2 × ArH), 7.4–7.0 (m, 13 × ArH), 6.6 (m, 2 × ArH), 6.2–5.8 (m, =C*H*Ph), 5.3 (m, CH_2CH=), 3.6 (t, *J* 7 Hz, CH_2COCo), 1.9 (m, CH_2), and 1.5 (m, CH_2).

6-*Ethoxycarbonylhex-5-enoylcobalt*(III) *Salophen Complex* (**42b**).—According to the general procedure, ethyl 6-chlorocarbonylhex-2-enoate (5 mmol) was treated with sodium cobalt(I) salophen (**5**) (5 mmol) to give the acylcobalt complex (**42b**) (1.85 g, 60%) as a maroon solid; $\nu_{max}(CHCl_3)$ 1 720 cm^{-1}; δ_H 8.4 (2 × CH=N), 7.8–6.2 (m, 12 × ArH and CH=), 5.9–5.1 (m, =CH), 4.2 (m, OCH_2Me), 3.5 (t, *J* 6.4 Hz, CH_2COCo), 2.8–1.4 (m, 2 × CH_2), and 1.22 (m, OCH_2Me).

(E)- *and* (Z)-2-*Benzylidenecyclopentanone* (**43**).—A solution of the acylcobalt complex (**42a**) (0.62 g) in dry, deoxygenated dichloromethane (100 ml) was irradiated under reflux for 24 h under nitrogen. The solvent was evaporated off *in vacuo*, and the residue was then purified by column chromatography to give: (i) (Z)-2-*benzylidenecyclopentanone* (**43**) (eluted first) (76 mg, 44%) as a yellow oil; b.p. 104–106 °C at 0.5 mmHg; ν_{max}(EtOH) 302 nm (ε 19 140); $\nu_{max}(CHCl_3)$ 1 703, 1 610, and 1 160 cm^{-1}; δ_H 7.9–7.8 (m, 2 × ArH), 7.5–7.2 (3 × ArH), 6.7 (t, *J* 2.2 Hz, =C*H*Ph), 2.8 (dt, *J* 7.4 and 2.2 Hz, CH_2), 2.4 (t, *J* 7.7 Hz, CH_2), and 2.0 (quin, $J \sim J$ 7.4 Hz, CH_2); δ_C 205.8 (C=O), 136.3, 136.2, 134.8, 130.4, 129.2, 127.9, 41.0, 34.5, and 20.5 (Found: C, 83.3; H, 7.5%; M^+, 172.0883. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%; *M*, 172.0888) and (ii) (*E*)-benzylidenecyclopentanone (**43**) (eluted second) (48 mg, 28%) as a pale yellow solid, b.p. 110–112 °C at 0.4 mmHg (lit.,[27] 165–168 °C at 10 mmHg), which was crystallised from light petroleum as leaflets, m.p. 69–70 °C (lit., [27] 68–69 °C); ν_{max}(EtOH) 297 nm (39 110); $\nu_{max}(CHCl_3)$ 1 705, 1 625, and 1 173 cm^{-1}; δ_H 7.55–7.30 (m, Ph and =CH), 3.0 (dt, *J* 7.5 and 2.7 Hz, C=CCH_2), 2.41 (t, *J* 7.9 Hz, CH_2), and 2.0 (quin, $J \sim 7.5$ Hz, CH_2); δ_C 208.0 (C=O), 136.2, 135.7, 132.3, 130.6, 129.3, 128.8, 37.8, 29.4, and 20.3 (Found: M^+, 172.0890. Calc. $C_{12}H_{12}O$: *M*, 172.0888).

(Z)- *and* (E)-*Ethyl* (2-*Oxocyclopentylidene*)*acetate* (**45**), *Ethyl* (5-*Oxocyclopent*-1-*enyl*)*acetate, and Ethyl* (2-*Oxocyclopentyl*)-*acetate* (**44**).—A solution of the acylcobalt complex (**42b**) (0.40 g) in dry, deoxygenated dichloromethane (80 ml) was irradiated under reflux for 48 h under nitrogen. The solvent was evaported off *in vacuo*, and the residue was then purified by column chromatography to give: (i) a mixture of (*E*)- and (*Z*)-ethyl (2-oxocyclopentylidene)acetate (**45**) and ethyl (5-oxocyclopent-1-enyl)acetate (23 mg, 21%) (eluted first) as a pale yellow oil; $\nu_{max}(CHCl_3)$ 2 900, 1 710, and 1 638 cm^{-1}; δ_H 6.50 (t, *J* 3 Hz, =CH), 5.9 (t, *J* 1.5 Hz, =C*H*CO_2Et, *E*-isomer), 5.7 (t, *J* 1.5 Hz, =C*H*CO_2Et, *Z*-isomer), 4.2 (m, OCH_2Me), 3.1 (dt, *J* 7.8 and 3 Hz, CH_2), 2.6–1.5 (m, 2 × CH_2), 1.3 (m, OCH_2Me) (Found: M^+, 168.0766. $C_9H_{12}O_3$ requires *M*, 168.0786) and (ii) *ethyl* (2-*oxocyclopentyl*)*acetate* (**44**) (eluted second) (30 mg, 28%) as a yellow oil; $\nu_{max}(CHCl_3)$ 2 940, 2 890, and 1 720 cm^{-1}; δ_H 4.1 (q, *J* 7.1 Hz, OCH_2Me), 2.7 (m, CH), 2.5–2.0 (m, $[CH_2]_2$), 1.9–1.6 (m, CH_2), and 1.3 (t, *J* 7.1 Hz, OCH_2Me); $\delta_C(CDCl_3)$ 219.2, 172.1, 60.6, 45.7, 37.5, 34.1, 29.3, 20.7, and 14.2 (Found: M^+, 170.0900. $C_9H_{14}O_3$ requires *M*, 170.0943).

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