Cobalt-mediated Reactions: Inter- and Intra-molecular Additions of Carbamoyl Radicals to Alkenes in the Synthesis of Amides and Lactams

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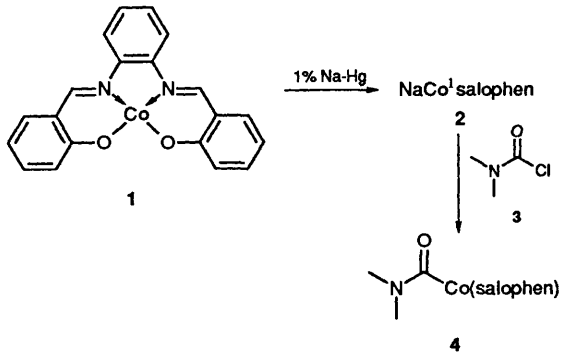
Carbamoylcobalt(III) salophen compounds, such as **4**, are sources of carbamoyl radicals under either thermal or photolytic conditions. Generation of *N,N*-dimethylcarbamoyl radicals, *e.g.* **5**, in the presence of trapping agents such as diphenyl disulfide or 2,2,6,6-tetramethylpiperidin-1-yloxy radical **7** afforded the expected amido derivatives, *e.g.* **6** and **8**, respectively. These radicals **5** also underwent oxidative intermolecular addition to styrene; the thermal process gave the *E*-cinnamide **10** exclusively, whereas under photochemical conditions a 1:1 mixture of *E*- and *Z*-cinnamides, **10** and **11**, respectively, was obtained. A series of *N*-alkenyl-*N*-alkylcarbamoylcobalt(III) salophens have also been prepared (*i.e.* **14**, **33** and **43**), and are shown to be suitable precursors for the synthesis of β-, γ- and δ-lactams through the 4-, 5- or 6-*exo-trig*-modes of cyclisation of the corresponding intermediate carbamoyl radicals. The products of these cyclisations, *N*-alkyl-3-lactamidomethyl radical (*i.e.* **16**, **34** or **46**) are trapped by the cobalt(II) salophen to give the corresponding alkylcobalt(III) salophens (*e.g.* **16**→**17**). Although these alkylcobalt salophens appeared to be stable at temperatures ≤40 °C, under the thermolytic conditions for radical generation that were usually employed (110 °C) dehydrocobaltation occurred, and the unsaturated lactam was formed. Results concerning the introduction of side-chain oxygen functionality at the product radical centre in tandem with the carbamoyl radical cyclisation are also presented. Computer-generated molecular modelling calculations supporting the novel 4-*exo-trig*-cyclisation of **15** are discussed.

In earlier work we have described the use of acylcobalt salophen reagents as sources of acyl radicals.[1] These acyl radicals were then shown to add successfully in both the inter- and intramolecular senses to activated C=C, thereby providing a convenient route to either enones or saturated ketones (depending upon the nature of the quenching steps involving the intermediate radical adducts). The scope for this relatively simple procedure would be greatly extended if it proved possible likewise to generate heteroatom-substituted acyl radicals. Assuming that the substituted acyl radicals possessed similar reactivity, this strategy would then allow a rather direct access to a variety of cyclic and acyclic compounds of synthetic interest, such as lactones, amides and lactams.

Lactams are well known to be essential constituents in a diverse range of natural and non-natural products of chemotherapeutic interest. The β-lactam family for example, has acquired a status of unparalleled importance and significance in modern times in the treatment of infectious diseases caused by bacteria.[2,3] It is therefore not surprising that β-lactams have provided a challenge to both synthetic chemists (in the design of new approaches to the azetidin-2-one ring system)[4] and medicinal chemists (in the search for novel, more active analogues). Both γ- and δ-lactams have been less well investigated, but these ring systems are also of interest—especially those α-methylene derivatives[5] which resemble the well-known naturally occurring anti-tumoral α-methylene-γ-butyrolactones.[6] Our attention, therefore, focussed upon the synthesis of carbamoylcobalt(III) salophens, and we now describe the results of the applications of these reagents to the synthesis of amides and of β-, γ- and δ-lactams.[7]

Carbamoyl radicals have been studied only in the last 30 years. Elad and Rokach demonstrated that the radical species produced from the photolysis of formamide added to both terminal and non-terminal alkenes.[8a,b] The addition to norbornene was stereospecific in that only *exo*-norbornylcarboxyamide was formed.[8c] Wender and Singh have employed a formamide-derived radical in their novel synthesis of the pentacyclic sesterterpene (−)-retigeranic acid, a lichen metabolite.[9] Carbamoyl radicals have also been observed in ESR studies,[10] and subsequent work has demonstrated that *N*-alkylcarbamoyl radicals exist in both *E*- and *Z*-conformations.[11] *N*-Arylcarbamoyl radicals (ArNHC˙=O), where the aromatic ring is almost coplanar with the amide plane, are known only as transient species since decarbonylations are rapid to give the more persistent aminyl (ArNH˙) and nitroxyl (ArNH–O˙) radical species. Coplanarity is no longer attainable in *N*-aryl-*N*-alkyl-carbamoyl radicals, and these species are sufficiently persistent to be detected directly by ESR.[12]

Intermolecular Reactions.—We commenced our investigations with the commercially available *N,N*-dimethylcarbamoyl chloride **3** as a convenient substrate for generating carbamoylcobalt compounds and hence carbamoyl radicals. Thus, treatment of **3** with sodium cobalt(I) salophen **2**[13] afforded the carbamoylcobalt(III) compound **4**[14] as a deep red crystalline solid in 50% yield (Scheme 1). The whole reaction is simply

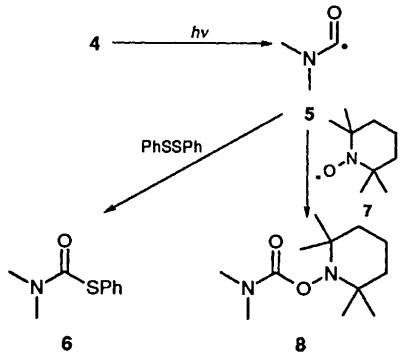


Scheme 1

monitored by a succession of colour changes. The almost black solution of cobalt(II) salophen **1** turns the characteristic green colour of sodium cobalt(I) salophen **2** on reduction with 1% sodium amalgam. The green solution of **2**, which is highly

sensitive to oxygen although stable at room temperature under an inert atmosphere, was changed to a reddish brown colour upon acylation to give **4**. The carbamoylcobalt derivative **4** was stable at room temperature in daylight, but was somewhat unstable on alumina and highly unstable on silica gel. The deep red colour of the crystalline material is distinctive of acylcobalt(III) salophens.[1,15,16]

A deoxygenated solution of **4** in dichloromethane containing 2 equiv. of diphenyl disulfide when irradiated with a 300 W health lamp (reflux, 48 h) afforded the sulfide **6** (46%).[17] The production of **6** is consistent with the operation of an S_H2 mechanism in which the intermediate *N*,*N*-dimethylcarbamoyl radical **5**, produced by homolysis of **4**, induces the decomposition of the disulfide (Scheme 2). However, two other

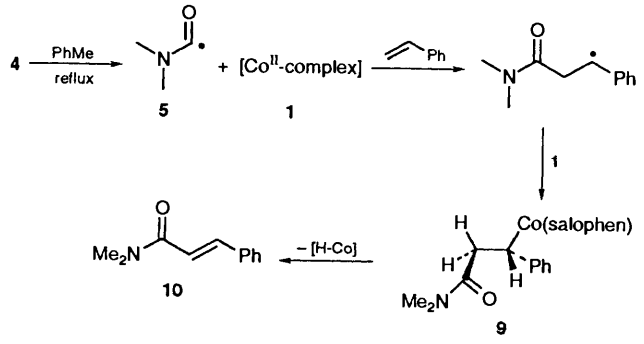


Scheme 2

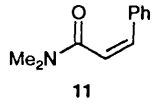
mechanisms are also feasible. The first, another S_H2 process, involves the attack of photochemically-generated PhS$^{\bullet}$ radicals[18a] on **4**, inducing the cleavage of the cobalt–carbon bond. The second, an S_H1 process, in which the **5** and PhS$^{\bullet}$ radicals simply combine, seems the least likely of the three mechanisms. Thermolysis of **4** in the presence of diphenyl disulfide in the dark in boiling toluene, a temperature that is rather too low for the homolysis of the S–S bond of the disulfide, also gave the sulfide **6**, albeit only in 16% yield. The adduct **6** could not be detected in thermolysis reactions run at a lower temperature (*e.g.* benzene, reflux), and the results therefore seem to favour the pathway shown in Scheme 2. Definitive evidence for the mechanisms of these cobalt-mediated reactions must await further investigation. Recent work on the radical chemistry of acylsilanes,[18b] acylgermanes,[18c] and acyltellurides,[18d] indicate that a variety of mechanisms are possible.

Irradiation of a boiling and deoxygenated dichloromethane solution of **4** containing 2,2,6,6-tetramethylpiperidin-1-yloxy radical **7** (TEMPO; 2 equiv.) for 20 h afforded the crystalline carbamate **8** (75%) as the sole product (Scheme 2). The related thermolytic process (toluene, reflux, 1 h) also gave **8** in excellent yield (81%). Two mechanisms seem possible in this case—the S_H1 process shown in Scheme 2, or an S_H2 mechanism in which TEMPO induces the decomposition of **4**. Although TEMPO is a stable radical, and therefore by definition is generally unreactive towards non-radical substrates, the bond dissociation energy of a C–Co^{III} bond amounts to only 20–30 kcal mol^{-1},[19] and such a homosolvolysis reaction[20] cannot be ruled out.

Having established that carbamoylcobalt(III) complexes are viable sources of carbamoyl radicals, we next investigated the addition of these species to C=C bonds as a means for the synthesis of amides and lactams. In intramolecular additions it is known that a variety of radicals can be added successfully to non-activated alkenes. However, in the slower intermolecular additions there are a number of potentially wasteful side-reactions: (i) H-abstraction, (ii) radical–cobalt^{II} complex recombination, (iii) radical dimerisation and (iv) decarbonylation. Hence, in common with previous precedence, we turned our attention towards the use of an alkene with a suitable radical-stabilising substituent, and styrene[17b,21] was first selected for this purpose. When a mixture of **4** and styrene (10 equiv.) was subjected to thermolytic conditions, the *E*-cinnamide **10** was the only product isolated (51%). The probable mechanism is summarised in Scheme 3. Under the photochemical conditions,



Scheme 3



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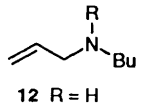
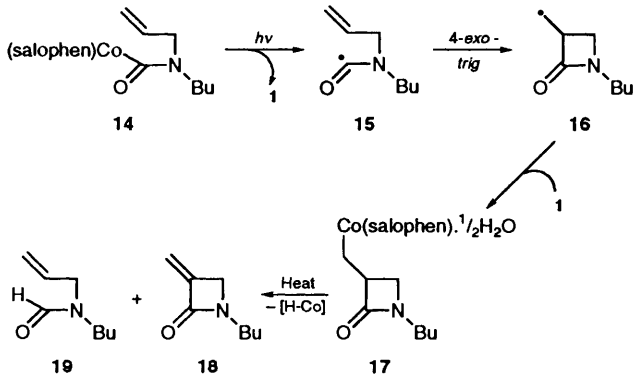
however, a 1:1 mixture of the *E*- and *Z*-cinnamides **10** and **11** were obtained in a combined yield of 41%. This result should be contrasted with Branchaud's results[17b] in which cobalt-mediated photoadditions of *alkyl* radicals onto styrene led exclusively to *E*-adducts, and compared with earlier results from our own group[21] where analogous reactions using *acyl* radicals gave rise to both *E*- and *Z*-adducts. It seems unlikely that the *Z*-cinnamide **11** would be formed by the *syn*-dehydrocobaltation of the more congested eclipsed conformer of **9** in the photochemical reaction but not in the (higher temperature) thermolytic process. Hence, a photoequilibration of **10** and **11**[22] appears to have occurred, but we were unable to demonstrate this interchange in the irradiation of a solution of **10** in the presence of a stoichiometric quantity of cobalt(II) salophen **1**.

Intramolecular Reactions.—We next examined the scope for intramolecular alkene additions of carbamoyl radicals with a view to the synthesis of a range of lactams. For the synthesis of β-lactams an allylamine was required, and volatility considerations dictated that *N*-allyl-*N*-butylamine **12** was the simplest member of this class that could be handled with comfort. Reaction of allyl bromide with butylamine first gave **12**,[23] which was next converted into the carbamoyl chloride **13** by reaction with bis(trichloromethyl) carbonate ('triphosgene'; 0.33 equiv.) and pyridine (1 equiv.) in dry benzene. Treatment of **13** with sodium cobalt(I) salophen **2** afforded the carbamoylcobalt(III) salophen **14** (57%) as a deep red crystalline solid.



12 R = H
13 R = COCl

Irradiation of a deoxygenated solution of **14** in dichloromethane for 48 h led to the formation not of the expected 3-methyleneazetidin-2-one **18**, but of the 3-(azetidin-2-one)methylcobalt(III) salophen **17**, isolated as a stable bright green solid (42%). The green colour is characteristic of alkylcobalt(III) salophen complexes, and the structure followed from the



Scheme 4

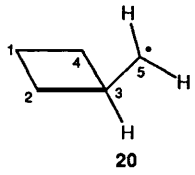
spectroscopic data—especially from the FAB mass spectrum and ^{1}H homonuclear and ^{1}H–^{13}C heteronuclear two-dimensional shift-correlation NMR experiments. The 0.5 equiv. of water (suggesting one water molecule sandwiched between two cobalt species, thereby complexing their available axial sites) was detected in the ^{1}H NMR spectrum, and confirmed by the microanalytical results for **17**. A mechanism for the formation of **17** is given in Scheme 4, a key feature being the 4-*exo-trig* cyclisation of the initially formed carbamoyl radical **15** to give the β-lactamidomethyl radical **16**; radical **16** is then trapped by the cobalt(II) salophen species to give **17**. The temperature of the photochemical reaction (40 °C) was presumably insufficient to promote *syn*-dehydrocobaltation leading to the strained azetidinone **18**. However, the conversion **17**→**18** was achieved in boiling toluene, albeit in only 21% yield. The formamide **19** was also isolated as a minor product (~2%).

Prior to our own investigations, we were aware of only one example of a 4-*exo-trig* radical cyclisation—which itself may be a special case because of a high degree of fluorine substitution.[24] However, these cyclisation processes should be favoured by stereoelectronic factors in that the angle α subtended by the three interacting atoms is maintained along the reaction pathway, and becomes the angle between these atoms in the product (Scheme 5).[25] Despite this favourability, Kaplan had observed the reverse of the process shown in Scheme 5, namely

Scheme 5

the fragmentation of a cyclobutylmethyl radical **20** to the corresponding pent-4-en-1-yl radical.[26] Beckwith has argued that such a fragmentation is aided if the p-orbital containing the unpaired electron [at C(5)] is able to achieve a coparallel orientation with respect to the σ*-orbital of a β/γ bond [*e.g.* C(3)–C(4)].[27] The driving force for fragmentation is the relief of ring strain, and ring-opening was considered to be irreversible. Both calculations at the MINDO/3 level,[28] and ESR results[29] have supported Beckwith's conclusions. More recently, however, Newcomb and his colleagues have demonstrated that pent-4-en-1-yl radicals undergo 4-*exo-trig* cyclisations when the resulting cyclobutylmethyl radicals were especially stabilised by substituents.[30]

In our own system the 4-*exo-trig* cyclisation leading to **16** appears to have occurred with extraordinary ease, yet **16** failed to fragment to the (presumably stabilised) amidomethyl radical **21** as would be expected from Beckwith's conclusions. In order to validate and analyse the results for our system, the product and reactant radicals from both reactions were geometry optimised using a standard semi-empirical MO method (AM1/UHF).[31,32] For the cyclobutylmethyl radical **20** geometry optimisation revealed a near square planar ring. It was clear, even in the ground state, that the singly occupied non-bonding MO (SOMO) mixed significantly with the ring C–C σ*-orbitals (the lowest anti-bonding levels), and the unpaired electron was partially delocalised into the ring by this mechanism. In addition, the bond which lined up with the SOMO was lengthened and weakened. In contrast, in the β-lactamidomethyl radical **22** geometry optimisation revealed a



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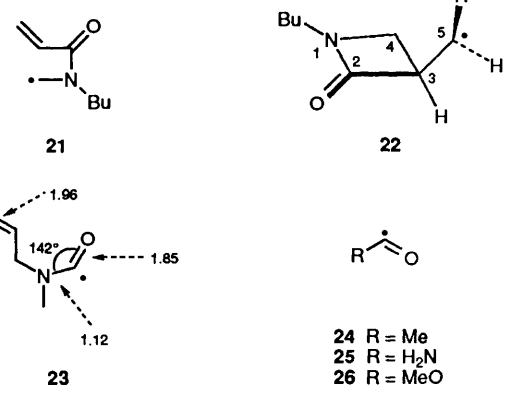
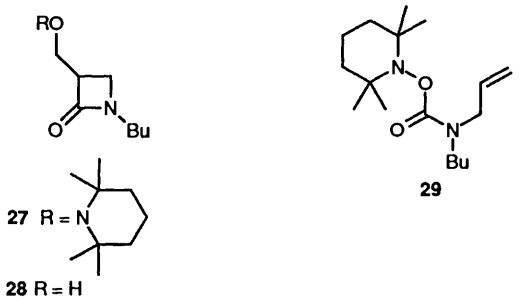


slightly non-planar ring, and the electron density (unpaired electron delocalisation) through the structure revealed a low value at C(4), the potential fragmentation position. There was no mixing of the SOMO and the ring C–C σ*-orbitals; instead, the SOMO appeared to mix with the N–C=O π*-system, which was of much lower energy than the σ*-orbitals. The interaction of the unpaired electron with the electrons in the N and C=O π-system stabilised the radical by *ca.* 0.5 eV (*i.e.* by *ca.* 12 kcal mol^{-1}). This provides some explanation of why the β-lactamidomethyl radical **22** does not fragment, and also supports the idea proposed by Beckwith and Moad[27] concerning the mechanism of the radical cleavage.

The carbamoyl radical (**23**) was itself also evaluated, and the significant bond orders and angles are as shown. The N–C–O angle of 142° is somewhat intermediate between a linear geometry (with the unpaired electron in a pure p-orbital) and a trigonal geometry (in which the unpaired electron is in a formal sp^2 hybridised orbital). The related angle for the series of acyl radicals **24**–**26** was calculated[32] to be in the range 140–144°. However, their thermodynamic stabilities varied greatly, with the alkoxy-acyl radical **26** being the most stable. One of the ester-oxygen lone pairs in **26** is delocalised into the C=O π*-system (as is the case for the nitrogen lone pair in **25**), and the extra stabilisation results from the mixing of the orbital containing the second lone pair with the orbital containing the unpaired electron.

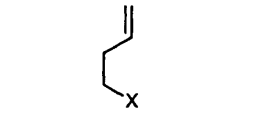
An important family of naturally occurring β-lactam antibiotics (*e.g.* thienamycin, see following paper) possess 1′-hydroxyalkyl side-chains in their C(3) position. Following on some established organo-cobalt chemistry,[33] the alkyl-cobalt(III) salophen **17** was converted smoothly into the azetidin-2-one **27** (71%) simply by heating a deoxygenated solution of the substrate in the presence of TEMPO **7**. The 3-methyleneazetidin-2-one **18** was also obtained as a minor by-product (4%). Under photolytic conditions, the adduct **27** was obtained



in 53% yield. Attempts to form **27** in tandem with cyclisation, through the irradiation of a solution of **14** in the presence of TEMPO, gave the adduct in only 3% yield. The major product was the acyclic carbamate **29** (69%), and presumably the rate constant for the 4-*exo-trig* cyclisation (which is estimated to lie in the range 0.1–1.0 s^{-1})[30] is significantly less than that for TEMPO trapping (especially if the trapping follows an S_H2 mechanism). Reductive hydrogenolysis (Pd–C, H_2, 7 d)[34] of **27** gave the desired alcohol **28** (70%) in addition to recovered **27** (17%).

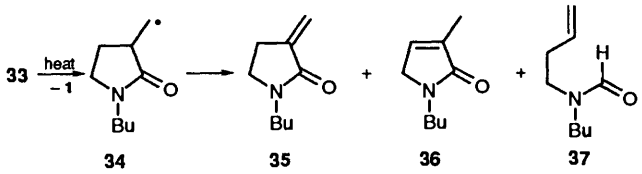
We next turned our attention towards the exploitation of the newly established carbamoyl radical cyclisation strategy in the synthesis of γ-lactams. The required precursor **33** was secured in three steps starting from 4-bromobut-1-ene **30**. Thus, **30** was treated with an excess of butylamine to give first **31** (84%) which was next transformed into the carbamoyl chloride **32** (97%) through reaction with triphosgene and pyridine. Reaction of **32** with sodium cobalt(I) salophen **2** then gave the carbamoylcobalt(III) salophen **33** (44%), a deep red crystalline solid. Interestingly, when **33** was isolated by column chromatography on alumina, trace quantities of a green compound were also isolated. Mass spectrometric analysis (FAB) revealed a molecular ion at *m/z* 527, and this green compound is thought to be the corresponding cyclic alkylcobalt(III) salophen resulting from ring closure of **33** (*cf.* **17**).

The homolytic cleavage of **33** was effected in boiling



30 X = Br
31 X = NHBu
32 X = N(Bu)COCl
33 X = N(Bu)COCo(salophen)

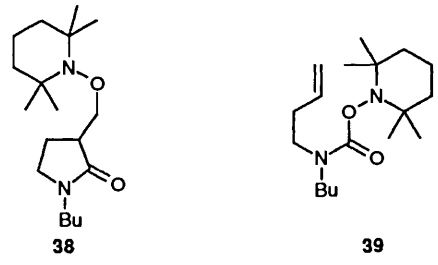
deoxygenated toluene (40 h), and chromatographic purification of the reaction products led to the isolation of the compounds **35**–**37** (Scheme 6). The γ-lactams **35** and **36**—which arise from



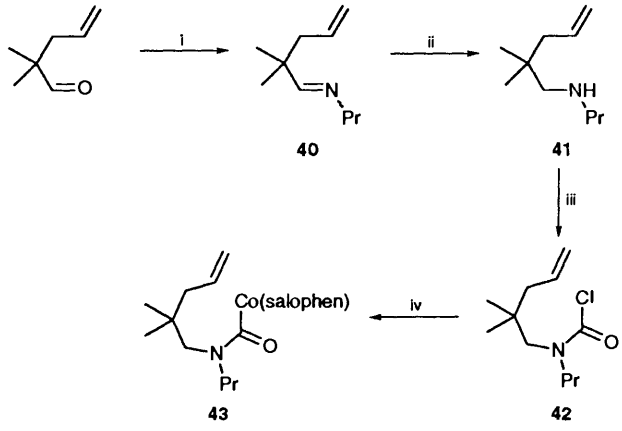
Scheme 6

the 5-*exo-trig* cyclisation of the intermediate carbamoyl radical, followed by trapping with cobalt(II) salophen, and then dehydrocobaltation—were isolated as a mixture of isomers (**35**:**36** = 6:1) in a combined yield of 64%. These isomers were separated by HPLC. The formamide **37** was obtained in 7% yield. When the cyclisation of **33** was conducted under photolytic conditions (CH_2Cl_2, reflux, 72 h), the same three products (**35**, **36** and **37**) were isolated in the respective yields 41, 14 and 6%. The proportion of **36** was, therefore, greater in the photochemical process, and it is possible that this results from a proportion of **35** becoming isomerised to **36** by a hydrocobaltation–dehydrocobaltation sequence. We were unable to demonstrate this conversion—*e.g.* irradiation of a solution of **35** in the presence of a stoichiometric amount of **1** failed to produce a detectable quantity of **36**—but, of course, this procedure does not pre-form the necessary hydridocobalt species.

We next attempted to introduce oxygen functionality in tandem with the aforementioned 5-*exo-trig* cyclisation, despite the lack of success achieved in the corresponding β-lactam series. Interestingly, irradiation, under the standard conditions, of a solution of **33** in the presence of TEMPO **7** led predominantly to the oxy-substituted γ-lactam **38** (59%) and the carbamate **39** (23%). It therefore appears that the 5-*exo-trig* cyclisation is marginally faster than the TEMPO trapping pathway.

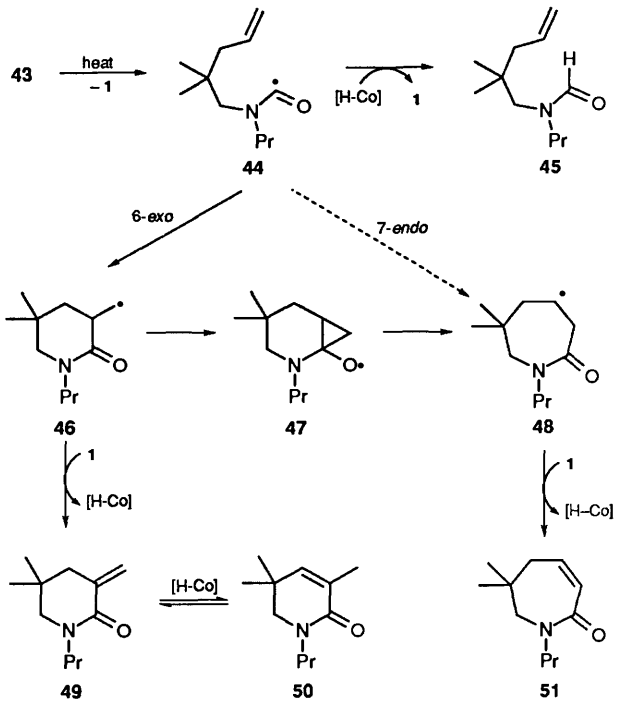


The homologous carbamoylcobalt(III) salophen compound **43** was prepared by the route shown in Scheme 7 whereby: (i)



Scheme 7 *Reagents:* i, $PrNH_2$, HCl–MeOH; ii, $NaCNBH_3$; iii, triphosgene, C_5H_5N; iv, **2**

2,2-dimethylpent-4-enal and propylamine were condensed to give the imine **40**; (ii) the imine was reduced with sodium cyanoborohydride to yield the secondary amine **41** (73% overall); (iii) the amine was converted into the carbamoyl chloride **42** (98%) using triphosgene; (iv) the chloride **42** was treated with sodium cobalt(I) salophen **2** to afford the carbamoylcobalt(III) compound **43** (44%), a deep red crystalline solid. Thermolysis of **43**, under the standard conditions, afforded the 3-methylenepiperidin-2-one **49** (51%), the isomeric δ-lactam **50** (7%), the formamide **45** (trace) and the tetrahydroazepin-2-one **51** (7%). In view of our previous results, the formation of three of the compounds (**45**, **49** and **50**) is unexceptional but **51** was unexpected. A possible mechanism is outlined in Scheme 8, and the tetrahydroazepin-2-one **51** is pictured as arising either from a 7-*endo-trig* cyclisation of the carbamoyl radical **44**, or through the radical addition–fragmentation pathway **46**→**47**→**48**. When the homolysis of **43**



Scheme 8

was conducted under standard photolytic conditions, the product ratio was **49** (32%), **50** (9%), **45** (2%) and **51** (trace).

Experimental

General Details.—A Reichert Kofler micro hot-stage was used for m.p. determinations which are uncorrected. IR spectra were recorded on a Perkin-Elmer 710B, Pye–Unicam SP3 100 or a Philips PU9706 spectrometer, and were calibrated using a standard polystyrene film; the spectra were recorded on thin films (for liquids) or chloroform solutions (for solids). UV spectra were obtained of solutions in spectroscopic grade ethanol using a Philips PU 8720 spectrophotometer. Unless stated otherwise, solutions in deuteriochloroform were used for the determination of NMR spectra. Shifts are expressed in ppm downfield from Me_4Si as internal standard. The ^1H and ^{13}C spectra were recorded on a 90 MHz Jeol FX90Q, 80 MHz Bruker WP80SY, 250 MHz Bruker WM250 or a 400 MHz Bruker AM400 instrument. Signals were singlets unless specified otherwise: *i.e.* d = doublet, dd = double doublet, ddd = double doublet of doublets, dt = double triplet, q = quartet, quint. = quintet, m = multiplet, br = broad. Assignments in the ^1H spectra were consistent with signal intensities and in the ^{13}C spectra with the results of the DEPT pulse sequence. Mass spectra were recorded on an AEI MS-902 or a MM-701CF instrument, using electron impact ionisation at 70 eV unless stated otherwise. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser.

Flash chromatography was performed using Merck silica gel 60, and the solvents light petroleum (b.p. 40–60 °C) and hexanes were redistilled before use. All reactions were monitored by TLC chromatography using Merck silica gel 60 F254 precoated aluminium plates. Solvents were purified and dried using standard procedures;[35] dry solvents were routinely stored under dry nitrogen. Organic extracts were dried over anhydrous magnesium sulfate and, after filtration, the solvent was removed using a Büchi rotary evaporator. Photolysis reactions were performed using an external Philips Ultraphil type KL 2866 (300 W) health lamp and standard Pyrex apparatus.

N,N′-o-*Phenylenebis(salicylideneaminato)cobalt*(II) [*Salophencobalt*(II)]* **1**.[13]—The flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (18.08 g, 72.6 mmol) in propanol (690 cm^3) was purged with nitrogen, and then warmed to 50 °C under a nitrogen atmosphere. *N,N′*-Bis(salicylidene)-*o*-phenylenediamine (22.55 g, 71.7 mmol) was added in one portion, and the resulting black suspension was then stirred and heated under reflux under a nitrogen atmosphere for 6 h. The mixture was then cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give black crystalline cobalt(II) salophen **1** (28.1 g, 100%).

Sodium Salophencobaltate(I) **2**.[13]—Mercury (40 g, 0.2 mol) was added with care to freshly cut small pieces of sodium (0.4 g, 17.7 mmol) under a flow of nitrogen. The reaction flask was swirled vigorously until an exothermic reaction was observed; slight warming with a Bunsen flame was occasionally necessary to initiate the reaction. The 1% sodium amalgam thus formed was allowed to cool to room temperature under nitrogen, and then added to a stirred and deoxygenated solution of salophencobalt(II) **1** (1.49 g, 4.0 mmol) in dry tetrahydrofuran (THF) (200 cm^3) at room temperature under an atmosphere of argon. The mixture was stirred for 1.5 h in the dark under argon, and then allowed to settle during 0.5 h. About 90% of the dark green solution of the title compound **2** was then transferred, using a cannula, into a dry argon-flushed flask. This material was used immediately.

N,N-*Dimethylcarbamoyl(salophen)cobalt*(III) **4**.[14]—Dimethylcarbamoyl chloride **3** (0.55 g, 0.5 cm^3, 5.43 mmol) was injected dropwise over 0.5 min into a stirred green solution of sodium (salophen)cobaltate(I)[13] **2** (2.05 g, 5.5 mmol) in dry deoxygenated THF (250 cm^3) in the dark under an atmosphere of nitrogen. The green colour of the solution was discharged, and the resulting brown solution was then stirred for a further 1 h in the dark under nitrogen. The solution was filtered under reduced pressure and the filtrate was then evaporated to dryness under reduced pressure in the dark at room temperature to leave a red–brown crystalline residue. The residue was pre-adsorbed onto Woelm alumina and purified by column chromatography over Woelm alumina in the dark (diethyl ether→dichloromethane) to yield the *title compound* **4** (1.21 g, 50%) as a deep red crystalline solid, m.p. > 100 °C (decomp); λ_{max}/nm 200 (ε/dm^3 mol^{-1} cm^{-1} 37 100), 254.5 (23 350), 296 (13 550) and 370 (9150); ν_{max}/cm^{-1} 3050, 2970, 1640, 1585, 1460, 1340, 1160 and 1090; δ_H(80 MHz) 8.8 (2 × HC=N), 8.05 (m, 2 × ArH), 7.6–7.2 (m, 8 × ArH), 6.8 (m, 2 × ArH), 3.2 (br s, Me) and 3.0 (Me); *m/z* (FAB) 445 (M, 16%), 374 [HCo(salophen), 37] and 72 [M − Co(salophen), 66].

S-*Phenyl* N,N-*Dimethylthiocarbamate* **6**.—(*a*) A boiling and deoxygenated solution of the carbamoyl(salophen)cobalt(III) **4** (222 mg, 0.5 mmol) and diphenyl disulfide (218 mg, 1 mmol) in dichloromethane (60 cm^3) was stirred and irradiated under an atmosphere of nitrogen for 48 h. The resulting mixture was cooled and then evaporated to dryness under reduced pressure to leave a brown residue. The residue was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether) to yield the *sulfide* **6** (42 mg, 46%) as a colourless oil; ν_{max}/cm^{-1} 3060, 2930, 2860, 1670 (CO), 1480, 1450, 1370, 1265, 1100 and 915; δ_H(80 MHz) 7.4 (m, 5 × ArH) and 3.0 (2 × Me); *m/z* 181.0547 (13%) ($C_9H_{11}NOS$

* For convenience, hereafter, salophen is used to refer to the coordinated ligand *N,N′-o*-phenylenebis(salicylideneaminato).

requires 181.0561), 151 (M − 2Me, 8), 109 (PhS, 13) and 72 (M − PhS, 100).

(*b*) When a deoxygenated solution of the carbamoylcobalt(III) salophen **4** (150 mg, 0.34 mmol) and diphenyl disulfide (147 mg, 0.67 mmol) in anhydrous toluene (25 cm^3) was stirred and heated under reflux for 24 h and then subjected to the above isolation and purification procedures, the sulfide **6** (9.5 mg, 16%) was obtained as a colourless oil.

2,2,6,6-*Tetramethylpiperidin*-1-*yl* N,N-*Dimethylcarbamate* **8**.—(*a*) TEMPO **7** (105 mg, 0.67 mmol) was added in one portion to a stirred solution of the carbamoyl(salophen)cobalt(III) **4** (150 mg, 0.34 mmol) in dry toluene (25 cm^3). The resulting solution was deoxygenated and then stirred and heated under reflux under an atmosphere of argon for 1 h. The mixture was cooled and the solvent then removed under reduced pressure to leave a brown solid residue. The residue was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:1) to give a colourless oil. The oil was further purified by Kugelröhr distillation, b.p. 140 °C/0.2 Torr, to yield, on cooling, the *carbamate* **8** (61 mg, 81%) as a white solid, m.p. 71–73 °C; ν_{max}/cm^{-1} 2980, 2940, 1740 (CO), 1470, 1385, 1270, 1155, 1025 and 770; δ_H(250 MHz) 2.95 (NMe_2), 1.8–1.3 (m, 3 × CH_2), 1.15 (2 × Me) and 1.1 (2 × Me); *m*/*z* 228 (1%), 213 (M − CH_3, 33), 156 (TEMPO, 4) and 72 (M − TEMPO, 100) (Found: C, 63.15; H, 10.35; N, 12.3%; M, 228.1816. $C_{12}H_{24}N_2O_2$ requires C, 63.1; H, 10.6; N, 12.25%; *M*, 228.1838).

(*b*) A boiling, deoxygenated solution of the carbamoyl(salophen)cobalt(III) **4** (163 mg, 0.37 mmol) and TEMPO **7** (114 mg, 0.73 mmol) in dichloromethane (150 cm^3) was irradiated under an atmosphere of nitrogen for 20 h and then subjected to the above isolation and purification procedures to give the carbamate **8** (63 mg, 75%) as a white solid, m.p. 71–73 °C; the spectroscopic properties were identical with those given above.

(E)-N,N-*Dimethylcinnamamide* **10** *and* (Z)-N,N-*Dimethylcinnamamide* **11**.—(*a*) A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **4** (140 mg, 0.314 mmol) and styrene (330 mg, 0.35 cm^3, 3.14 mmol) in dry toluene (25 cm^3) was stirred and heated under reflux under an atmosphere of nitrogen for 48 h. The mixture was cooled and the solvent removed under reduced pressure to leave a brown residue. The residue was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether) to give a yellow solid. The solid was recrystallised from diethyl ether to yield the *E*-cinnamamide **10** (28 mg, 51%) as a crystalline solid, m.p. 102–103 °C; λ_{max}/nm 205 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 16 150), 218 (17 100) and 279 (25 150) (*cf.* lit.,[22] 277 nm); ν_{max}/cm^{-1} 3060, 2980, 2940, 1650 (CO), 1610 (C=C), 1480, 1400, 1150 and 990; δ_H(80 MHz) 7.7 (d, *J* 15.5 Hz, PhC*H*=), 7.55–7.25 (m, 5 × ArH), 6.85 (d, *J* 15.5, =CHCO), 3.1 (br s, NMe) and 3.05 (br s, NMe); δ_C(100 MHz) 166.6 (CO), 142.1 (CH), 135.3 (quat. C), 129.5 (CH), 128.7 (CH), 127.7 (CH), 117.5 (CH), 37.3 (Me) and 35.8 (Me); *m*/*z* 175 (M, 38%), 131 (M − NMe_2, 100), 103 (M − Me_2NCO, 57) and 72 (M − HC=CHPh, 3) (Found: C, 75.45; H, 7.55; N, 7.7%; M, 175.0989. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%; *M*, 175.0997).

(*b*) A boiling and deoxygenated solution of the carbamoyl(salophen)cobalt(III) **4** (110 mg, 0.21 mmol) and styrene (219 mg, 0.24 cm^3, 2.1 mmol) in dichloromethane (50 cm^3) was stirred and irradiated under an atmosphere of nitrogen for 48 h, and then subjected to the above isolation and purification procedures. The product (15 mg, 41%), a yellow solid, was obtained as a 1:1 mixture of the *E*-cinnamide (whose spectroscopic data were identical with those obtained previously) and the *Z*-*cinnamamide* **11**; λ_{max}/nm 200 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 15 050) and 266 (8700); δ_H(250 MHz) 7.55–7.25 (m, 5 × ArH), 6.65 (d, *J* 12.4, PhC*H*=), 6.05 (d, *J* 12.4, =CHCO), 3.0 (NMe) and 2.85 (NMe); *m*/*z* 175.1013 (40%) ($C_{11}H_{13}NO$ requires 175.0997), 131 (M − NMe_2, 100), 103 (M − Me_2NCO, 52) and 72 (M − HC=CHPh, 8).

N-*Allyl*-N-*butylamine* **12**.—3-Bromopropene (2.18 g, 1.5 cm^3, 18 mmol) was added dropwise over 3 min to stirred and cooled (0 °C) butylamine (9.5 cm^3, 182 mmol). The resulting mixture was stirred and heated under reflux for 20 h, and then cooled to 0 °C. Concentrated hydrochloric acid was added dropwise to it over 5 min until pH 1 was attained. Water (50 cm^3) was added to the resulting suspension, which was then washed with diethyl ether (2 × 50 cm^3). The remaining aqueous solution was cooled to 0 °C and then brought to pH 10 by slow addition of potassium hydroxide pellets. The liberated amine was extracted into diethyl ether (3 × 50 cm^3). The combined organic phases were dried, filtered and the solvent removed under reduced pressure at 2 °C to leave a pale yellow liquid. The liquid was further purified by Kugelröhr distillation to yield the amine **12** (1.13 g, 50%) as a colourless oil, b.p. 50 °C/30 Torr (*cf.* lit.,[23] 131 °C/760 Torr); ν_{max}/cm^{-1} 3090, 2970, 2940, 2880, 2820, 1645, 1460, 1130, 1000 and 925; δ_H(80 MHz) 6.2–5.7 (ddt, *J* 17.3, 9.9 and 5.9, =CH), 5.15 (br d, *J* 17.3, =C*H*H), 5.10 (br d, *J* 9.9, =CH*H*), 3.25 (dd, *J* 5.9 and 1.1, =CHCH_2), 2.65 (t, *J* 7.0, NCH_2CH_2), 1.7–1.1 (m, C$H_2CH_2CH_3$), 1.45 (NH) and 0.8–1.0 (t, *J* 6.3, Me).

N-*Allyl*-N-*butylcarbamoyl Chloride* **13**.—A solution of the amine **12** (1.01 g, 8.9 mmol) in dry benzene (4 cm^3) was added dropwise over 0.5 min to a stirred suspension of triphosgene (0.88 g, 2.97 mmol) and dry pyridine (708 mg, 8.92 mmol) in dry benzene (40 cm^3) under an atmosphere of nitrogen. The resulting suspension was stirred under nitrogen for 96 h. The suspension was filtered under nitrogen and the filtrate was then evaporated to dryness under reduced pressure to leave the *title compound* **13** (1.50 g, 96%) as a yellow liquid; ν_{max}/cm^{-1} 3100, 2980, 2940, 2880, 1735 (CO), 1640, 1460, 1405, 1360, 1210, 1180, 1130, 1100 and 940; δ_H(90 MHz) 6.15–5.65 (ddt, *J* 17.2, 9.8 and 6.0, =CH), 5.24 (br d, *J* 9.8, =C*H*H), 5.19 (br d, *J* 17.2, =CH*H*), 4.0 (t, *J* 6, =CHCH_2), 3.6–3.1 (br t, *J* 7.2, NCH_2CH_2), 1.85–1.15 (m, C$H_2CH_2CH_3$) and 1.05–0.9 (t, *J* 7.3, Me).

N-*Allyl*-N-*butylcarbamoyl*(*salophen*)*cobalt*(III) **14**.—A deoxygenated solution of the carbamoyl chloride **13** (0.75 g, 4.3 mmol) in dry THF (10 cm^3) was added dropwise over 1 min to a stirred and deoxygenated green solution of sodium cobalt(I) salophen **2** (4.9 mmol) in anhydrous THF (200 cm^3) in the dark under an atmosphere of argon. The resulting brown solution was stirred for 1 h in the dark under argon, and then filtered under reduced pressure. The filtrate was evaporated to dryness under reduced pressure in the dark at ambient temperature to leave a red–brown solid residue. The residue was pre-adsorbed onto Woelm alumina and then purified by column chromatography over Woelm alumina (diethyl ether→methanol–ethyl acetate, 1:100) to yield the *title compound* **14** (1.25 g, 57%) as a deep red crystalline solid, m.p. > 100 °C (decomp.); λ_{max}/nm 200 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 40 000), 230 (30 600), 258 (30 700), 299 (19 600) and 368 (15 000); ν_{max}/cm^{-1} 2940, 2870, 1645sh (CO), 1610, 1580, 1460, 1440, 1380, 1340 and 1155; δ_H(80 MHz) 8.75 (2 × HC=N), 8.1–7.9 (m, 2 × ArH), 7.5–7.1 (m, 8 × ArH), 6.85–6.6 (m, 2 × ArH), 5.75–5.1 (br m, =CH), 5.0–4.7 (br m, =CH_2), 4.7–4.2 (br m, =CHCH_2), 3.6–3.1 (br m, NCH_2CH_2) and 1.3–0.4 (br m, C$H_2CH_2CH_3$); *m*/*z* (FAB) 513 (M, 37%), 373 [Co(salophen), 82] and 140 [M − Co(salophen), 41].

1-*Butyl*-2-*oxoazetidin*-3-*ylmethyl*(*salophen*)*cobalt*(III) *Hemihydrate* **17**.—A boiling and deoxygenated solution of the

carbamoyl(salophen)cobalt(III) **14** (300 mg, 0.58 mmol) and pyridine (46 mg, 0.58 mmol) in dichloromethane (35 cm^3) was stirred and irradiated under nitrogen for 48 h. The resulting green solution was cooled, then pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 2:1→ethyl acetate) to give: (i) the azetidin-2-one **18** (~ 1 mg) as a pale yellow oil, and: (ii) the *title compound* **17** (126 mg, 42%) as a deep green crystalline solid. The solid recrystallised from dichloromethane–hexanes as deep green crystals, m.p. 101 °C (decomp.); λ_{max}/nm 202 (ε/dm^3 mol^{-1} cm^{-1} 41 700), 234 (38 800), 306 (17 800) and 398 (14 160); ν_{max}/cm^{-1} 3400br, 2920, 2860, 1720 (CO), 1610, 1580, 1460, 1430, 1370, 1335, 1155, 1135 and 910; δ_H(400 MHz—assignments made from ^1H homonuclear and ^1H–^{13}C heteronuclear two-dimensional shift correlation experiments) 8.45 (HC=N), 8.35 (HC=N), 7.65 (br dd, *J* 10.0 and 8.2, 2 × ArH), 7.4–7.25 (m, 4 × ArH), 7.2 (dd, *J* 11.0 and 8.2, 2 × ArH), 7.0 (br s, 2 × ArH), 6.6 (m, 2 × ArH), 3.35 (br s, 0.5 H_2O), 3.0 (d, *J* 2.8, ring-CH_2), 2.95 (m, NCH_2CH_2), 2.9 [dd (*ca.* t), *J* 6.6 and 6.5, CoC*H*H], 2.45 (dd, *J* 6.2 and 3.6, CoCH*H*), 1.95 [ddt (*ca.* dq), *J* 6.8, 3.2 and 3.2, COCH], 1.3 (quint., *J* 7.1, CH_2CH_2-CH_3), 1.1 (sextet, *J* 7.3, CH_2CH_3) and 0.75 (t, *J* 7.2, Me); δ_C(100 MHz—assignments made from ^{13}C–^1H heteronuclear two-dimensional shift correlation experiments) 167.7 (quat. C), 167.6 (quat. C), 162.4 (CO), 155.8 (N=CH), 155.7 (N=CH), 144.1 (quat. C), 144.0 (quat. C), 134.8 (CH), 134.6 (CH), 134.1 (2 × CH), 127.0 (2 × CH), 124.1 (CH), 124.0 (CH), 119.7 (quat. C), 119.5 (quat. C), 116.4 (CH), 116.1 (CH), 114.6 (CH), 114.4 (CH), 55.0 (CO*C*H), 46.9 (ring CH_2), 41.1 (NCH_2), 29.4 (CH_2), 20.0 (CH_2), 13.6 (CH_3) and 13.5 ($CoCH_2$); *m*/*z* (FAB) 514 (M + 1, 28%), 513 (M, 24), 374 [Co(salophen) + 1, 46], 373 [Co(salophen), 35] and 140 [M − Co(salophen), 12] (Found: C, 64.3; H, 5.65; N, 7.65%. $C_{28}H_{28}N_3O_3Co$. 0.5 H_2O requires C, 64.35; H, 5.55; N, 8.05%).

N-*Butyl*-3-*methyleneazetidin*-2-*one* **18** *and* N-*Allyl*-N-*butylformamide* **19**.—A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **14** (569 mg, 1.11 mmol) in freshly distilled dry toluene (50 cm^3) was stirred and heated under reflux under an atmosphere of nitrogen for 48 h. The resulting mixture was cooled and then evaporated to dryness under reduced pressure to leave a brown solid residue. The residue was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:2) to give: (i) the *formamide* **19** (3.8 mg, 2.5%) (eluted first) as a pale yellow oil; ν_{max}/cm^{-1} 3060, 2920, 2870, 1660 (CO), 1420, 1400, 1180, 1130, 1000 and 935; δ_H(80 MHz) 8.1 (CHO), 6.0–5.5 (m, =CH), 5.30–5.05 (m, $=CH_2$), 3.95 and 3.80 (each d, *J* 6.0, $=CHCH_2$), 3.30 and 3.20 (each t, *J* 7.1, NCH_2CH_2), 1.80–1.05 (m, $CH_2CH_2CH_3$) and 0.90 (t, *J* 6.8, Me); *m*/*z* 141.1143 (20%) ($C_8H_{15}NO$ requires 141.1154), 126 (M − Me, 19), 112 (M − C_2H_5, 18) and 98 (M − C_3H_7, 100) and: (ii) an oil, which was further purified by Kugelröhr distillation, to afford the *azetidin*-2-*one* **18** (31.3 mg, 20.5%) as a colourless oil, b.p. 50 °C/0.5 Torr; λ_{max}/nm 199 (ε/dm^3 mol^{-1} cm^{-1} 13 750) and 240 (3350); ν_{max}/cm^{-1} 3040, 2940, 2870, 1740 (CO), 1670, 1460, 1400, 1320, 1080 and 930; δ_H(400 MHz) 5.7 (dd, *J* 3.0 and 1.2, =C*H*H), 5.15 (d, *J* 1.2, =CH*H*), 3.75 (*ca.* t, *J* 1.2, ring-CH_2), 3.35 (t, *J* 7.2, NCH_2CH_2), 1.55 (*ca.* quint., *J* 7.2, $CH_2CH_2CH_3$), 1.35 (*ca.* sextet, *J* 7.3, CH_2CH_3) and 0.95 (t, *J* 7.3, Me); δ_C(22.5 MHz) 163.6 (CO), 145.3 (=C), 108.7 ($=CH_2$), 48.2 (ring-CH_2), 41.6 (NCH_2), 29.8 (CH_2), 20.2 (CH_2) and 13.6 (CH_3); *m*/*z* 139.0987 (8%) ($C_8H_{13}NO$ requires 139.0997), 124 (M − CH_3, 7) and 96 (M − C_3H_7, 100).

1-*Butyl*-3-(2,2,6,6-*tetramethylpiperidin*-1-*yloxymethyl*)*azetidin*-2-*one* **27**.—(*a*) A deoxygenated solution of the methylazetidin-2-onecobalt(III) **17** (110 mg, 0.21 mmol) and TEMPO **7** (678 mg, 0.42 mmol) in dry toluene (25 cm^3) was stirred and heated under reflux under an atmosphere of nitrogen for 45 min. The mixture was cooled and then evaporated to dryness under reduced pressure to leave a brown solid residue. The residue was pre-adsorbed onto silica gel and then purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:1) to give: (i) the azetidin-2-one **19** (1.3 mg, 4%) (eluted first) as a colourless oil whose spectroscopic data were identical with those obtained previously, and: (ii) the *azetidin*-2-*one* **27** (44.6 mg, 71%) as a colourless oil; ν_{max}/cm^{-1} 2940, 2870, 1740 (CO), 1470, 1415, 1380, 1365, 1180, 1130, 1030 and 930; δ_H(400 MHz—assignments made from ^1H homonuclear two-dimensional shift correlation experiments) 4.1 (dd, *J* 9.5 and 4.7, CH*H*O), 4.0 (dd, *J* 9.5 and 3.2 Hz, C*H*HO), 3.35 (dt, *J* 14.0 and 7.2, NC*H*HCH_2), 3.35–3.25 (m, $CHCH_2$), 3.10 [dt (*ca.* quint.), *J* 13.9 and 6.7, NCH*H*CH_2], 1.60–1.50 (quint., *J* 7.2, $CH_2CH_2CH_3$), 1.50–1.30 [m, $(CH_2)_3$], 1.40–1.30 (sextet, *J* 7.1, CH_2CH_3), 1.20 (Me), 1.15 (Me), 1.10 (Me), 1.05 (Me) and 0.9 (t, *J* 7.3, CH_2CH_3); δ_C(100 MHz) 168.0 (CO), 71.9 (OCH_2), 60.1 (quat. C), 59.9 (quat. C), 49.3 (O=C*C*H), 42.7 (CH*C*H_2), 41.3 (NCH_2), 39.6 (CH_2), 33.2 (CH_3), 32.9 (CH_3), 29.7 (CH_2), 20.1 (CH_3), 20.1 (CH_2), 20.0 (CH_3), 17.0 (CH_2) and 13.7 (CH_3); *m*/*z* 296.2421 (0.5%) ($C_{17}H_{32}N_2O_2$ requires 296.2464); *m*/*z* (FAB) 297 (M + 1, 21), 281 (M − CH_3, 11), 156 (TEMPO, 6) and 140 (M − TEMPO, 39) (Found: C, 69.15; H, 10.75; N, 9.3%. $C_{17}H_{32}N_2O_2$ requires C, 68.85; H, 10.9; N, 9.45%).

(*b*) When a deoxygenated solution of the methylazetidin-2-onecobalt **17** (235 mg, 0.49 mmol) and TEMPO **7** (91 mg, 0.59 mmol) in dichloromethane (150 cm^3) was stirred and irradiated under reflux under an atmosphere of nitrogen for 40 h, both the azetidin-2-one **18** (1.1 mg, 1.5%) and the azetidin-2-one **27** (77 mg, 53.5%) were obtained as colourless oils whose spectroscopic data were identical with those obtained previously.

2,2,6,6-*Tetramethylpiperidin*-1-*yl* N-*Allyl*-N-*butylcarbamate* **29**.—A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **17** (300 mg, 0.58 mmol) and TEMPO **7** (100 mg, 0.64 mmol) in dichloromethane (150 cm^3) was stirred and irradiated under reflux under an atmosphere of nitrogen for 24 h. The mixture was cooled and then pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:2) to yield the *carbamate* **29** (119 mg, 69%) as a colourless oil; ν_{max}/cm^{-1} 3080, 3000sh, 2960, 2930, 2875, 1725 (CO), 1640, 1465, 1405, 1480, 1460, 1250, 1225, 1140, 1050 and 925; δ_H(80 MHz) 6.05–5.45 (ddt, *J* 17.4, 9.5 and 5.3, =CH), 5.25–4.90 (br m, $=CH_2$), 3.90–3.70 (br d, *J* 5.3, $=CHCH_2$), 3.18 (br t, *J* 7.1, NCH_2CH_2), 1.85–1.20 [br m, $CH_2CH_2CH_3$ and $(CH_2)_3$], 1.05 (2 × Me), 1.00 (2 × Me) and 0.85 (br t, *J* 7.0, CH_2CH_3); δ_C(20 MHz) 156.8 (CO), 133.9 (=CH), 115.9 ($=CH_2$), 59.7 (quat. C), 49.3 ($=CHCH_2$), 46.4 (CH_2), 38.9 (CH_2), 31.5 (CH_3), 30.2 (CH_2), 20.8 (CH_3), 19.7 (CH_2), 16.8 (CH_2) and 13.5 (CH_3); *m*/*z* 296.2522 (0.5%) ($C_{17}H_{32}N_2O_2$ requires 296.2464), 156 (TEMPO, 4) and 140 (M − TEMPO, 48). Further chromatography (diethyl ether–light petroleum, 2:1) gave the azetidin-2-one **18** (5.5 mg, 3%) as a pale yellow oil whose spectroscopic data were identical with those obtained previously.

1-*Butyl*-3-*hydroxymethylazetidin*-2-*one* **28**.—A flask containing a stirred solution of the TEMPO derivative **27** (27 mg, 0.091 mmol) in methanol (2 cm^3) was flushed with nitrogen, after which the stirring was stopped and 10% palladium on carbon catalyst (150 mg) was added to it. The flask was flushed with hydrogen and the mixture then stirred under an atmosphere of this for 8 d. The flask was flushed with nitrogen, and the mixture then filtered through Celite. The filtrate was evaporated to dryness under reduced pressure to leave an oil. The oil was purified by column chromatography over silica gel

(diethyl ether→ethyl acetate) to give: (i) starting material (5 mg, 19%), and: (ii) the *hydroxymethylazetidin-2-one* **28** (10 mg, 70%) as a colourless oil; ν_{max}/cm^{-1} 3400br, 2925, 2875, 1725 (CO), 1600, 1460, 1410, 1375, 1120, 1090, 1025, 970 and 910; δ_H(400 MHz) 4.0 (br dd, *J* 11.5 and 4.6, OC*H*H), 3.85 (br dd, *J* 11.5 and 4.2, OCH*H*), 3.35 [dddd (*ca.* dq), *J* 5.1, 4.6, 4.2 and 2.2, COCH], 3.3 [dd, (*ca.* t), *J* 5.1 and 5.1, ring C*H*H], 3.25 (dd, *J* 5.1 and 2.2, ring CH*H*), 3.25 (dt, *J* 14.8 and 7.2, NC*H*HCH$_2$), 3.2 (dt, *J* 14.8 and 7.2, NCH*H*CH$_2$), 2.45 (br s, OH), 1.5 (quint., *J* 7.2, CH_2CH$_2$CH$_3$), 1.35 (sextet, *J* 7.3, CH_2CH$_3$) and 0.95 (t, *J* 7.3, CH$_3$); δ_C(100 MHz) 168.6 (CO), 59.6 (OCH$_2$), 51.6 (ring CH), 42.2 (ring CH$_2$), 41.5 (NCH$_2$), 29.7 (CH$_2$), 20.1 (CH$_2$) and 13.65 (CH$_3$); *m/z* 157.1110 (8%) ($C_8H_{15}NO_2$ requires 157.1103), 139 (M − H_2O, 11), 128 (M − C_2H_5, 12), 114 (M − C_3H_7, 30) and 100 (M − C_4H_9, 19).

N-*But*-3-*enyl*-N-*butylamine* **31**.—4-Bromobutene **30** (2.02 g, 1.53 cm^3, 15 mmol) was added dropwise over 1 min to freshly distilled and stirred butylamine (14.8 cm^3, 150 mmol) at room temperature. The resulting solution was stirred and heated under reflux for 24 h and then cooled to 0 °C. Concentrated hydrochloric acid was then added dropwise to the mixture until it attained pH 1. After dilution with water (20 cm^3) the solution was extracted with diethyl ether (3 × 20 cm^3). The aqueous solution remaining after the extraction was cooled to 0 °C and then brought to pH 10 by the slow addition of potassium hydroxide pellets. The liberated amine was extracted with diethyl ether (4 × 50 cm^3). The organic phases were combined, dried, filtered and then evaporated to dryness under reduced pressure to leave a yellow oil. The oil was purified by Kugelröhr distillation to give the *amine* **31** (1.60 g, 84%) as a colourless liquid, b.p. 100 °C/30 Torr; ν_{max}/cm^{-1} 3090, 2965, 2940, 2880, 2820, 1640, 1470, 1140, 1005 and 920; δ_H(80 MHz) 5.95–5.45 (ddt, *J* 17.2, 9.8 and 6.6, =CH), 4.97 (br d, *J* 17.2, =C*H*H), 4.90 (br d, *J* 9.8, =CH*H*), 2.6 (t, *J* 6.5, =CHCH$_2$CH_2), 2.5 (t, *J* 6.6, NCH_2CH$_2$), 2.15 [ddt (*ca.* dq), *J* 6.6, 6.5 and 1.0, =CHCH_2], 1.5–1.05 (m, CH_2CH_2CH$_3$), 1.0 (NH) and 0.8 (t, *J* 7.3, CH$_2$CH_3); δ_C(20 MHz) 136.3 (=CH), 115.8 (=CH$_2$), 49.3 (NCH_2CH$_2$-CH=), 48.7 (NCH$_2$), 34.1 (CH_2CH=), 32.1 (CH$_2$), 20.25 (CH$_2$) and 13.7 (CH$_3$); *m/z* 127 (M, 0.4%), 113 (M − CH$_2$, 5) and 86 (M − C_3H_5, 100) (Found: C, 75.0; H, 13.9; N, 10.85%; M, 127.1358. $C_8H_{17}N$ requires C, 75.5; H, 13.5; N, 11.0%; *M*, 127.1361).

N-*But*-3-*enyl*-N-*butylcarbamoyl Chloride* **32**.—A solution of the amine **31** (1.55 g, 12 mmol) in dry benzene (5 cm^3) was added dropwise over 1 min to a stirred suspension of dry pyridine (0.98 g, 12 mmol) and triphosgene (1.20 g, 4.06 mmol) in dry benzene (45 cm^3) under an atmosphere of nitrogen. The resulting suspension was stirred under nitrogen for 96 h, and then filtered under nitrogen. The filtrate was evaporated to dryness under reduced pressure to leave the *carbamoyl chloride* **32** (2.2 g, 97%) as a yellow liquid; ν_{max}/cm^{-1} 3100, 2980, 2960, 2900, 1745 (CO), 1650, 1480, 1410, 1260, 1215 and 1125; δ_H(80 MHz) 6.05–5.55 (ddt, *J* 17.4, 9.6 and 6.6, =CH), 5.12 (br d, *J* 17.4, =C*H*H), 5.10 (br d, *J* 9.6, =CH*H*), 3.65–3.2 (br m, CH_2NCH_2), 2.6–2.2 [m (*ca.* q), =CHCH_2], 1.8–1.15 (m, CH_2CH_2CH$_3$) and 0.95 (t, *J* 7.2, CH$_2$CH_3).

N-*But*-3-*enyl*-N-*butylcarbamoyl*(*salophen*)*cobalt*(III) **33**.—A deoxygenated solution of the carbamoyl chloride **32** (379 mg, 2.0 mmol) in dry THF (10 cm^3) was injected over 1 min into a stirred green solution of the sodium salt **2** (2.0 mmol) in dry, deoxygenated THF (200 cm^3) in the dark under an atmosphere of argon. The resulting brown solution was stirred for 1 h and then, under reduced pressure, both filtered and evaporated to dryness in the dark at room temperature to leave a red–brown solid residue. This was pre-adsorbed onto Woelm alumina and purified by column chromatography over Woelm alumina (dichloromethane) to yield the *title complex* **33** (467 mg, 44%) as a deep red crystalline solid, m.p. > 100 °C (decomp.); λ_{max}/nm 198 (ε/dm^3 mol^{-1} cm^{-1} 38 700), 256 (21 300), 297 (12 050) and 357 (7900); ν_{max}3040, 2980, 1640sh (CO), 1610, 1580, 1465, 1440, 1375, 1335 and 1155; δ_H(80 MHz) 8.7 (2 × HC=N), 7.95 (m, 2 × ArH), 7.5–7.1 (m, 8 × ArH), 6.7 (m, 2 × ArH), 6.1–5.3 (br m, =CH), 5.1–4.5 (br m, =CH$_2$), 4.1–3.0 (br m, CH_2NCH_2), 2.1–1.7 (br m, =CHCH_2) and 1.4–0.4 (br m, CH_2CH_2CH_3); *m/z* (FAB) 1055 (2M + 1, 9%), 528 (M + 1, 38), 374 [Co(salophen) + 1, 100)] and 154 [M − Co(salophen), 61].

1-*Butyl*-3-*methylenepyrrolidin*-2-*one* **35**, 1-*Butyl*-3-*methyl*-1H-*pyrrol*-2(5H)-*one* **36** *and* N-*But*-3-*enyl*-N-*butylformamide* **37**.—(*a*) A deoxygenated solution of the carbamoyl(salophen)-cobalt **33** (223 mg, 0.42 mmol) in dry toluene (25 cm^3) was stirred and heated under reflux under an atmosphere of nitrogen for 40 h. The resulting mixture was cooled and then evaporated to dryness under reduced pressure to leave a brown solid residue. This was pre-adsorbed onto silica gel and then purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:1) to give: (i) the *formamide* **37** (4.5 mg, 7%), eluted first, as a pale yellow oil; ν_{max}/cm^{-1} 3080, 2965, 2940, 2880, 1670 (CO), 1425, 1395, 1215, 1120, 920 and 735; δ_H(80 MHz) 8.0 (br s, CHO), 6.0–5.4 (m, =CH), 5.2–4.9 (m, =CH$_2$), 3.4–3.0 (*ca.* br quint., *J* 7.1, CH_2NCH_2), 2.35–2.05 [dt (*ca.* q), *J* 7.0 and 7.0, =CHCH_2], 1.75–1.0 (m, CH_2CH_2CH$_3$) and 0.9 (t, *J* 6.6, CH$_3$); δ_C(20 MHz) 162.9 (CHO), 134.8 and 133.5 (=CH), 117.3 and 116.4 (=CH$_2$), 47.0 and 46.5 (NCH$_2$ allyl), 41.8 and 41.3 (NCH$_2$Pr), 32.9 and 31.4 (CH$_2$CH=), 30.2 and 29.1 (CH$_2$), 19.8 and 19.4 (CH$_2$), 13.5 and 13.4 (CH$_3$); *m/z* 155.1289 (5%) ($C_9H_{17}NO$ requires 155.1310) and 114 (M − C_3H_5, 25) and: (ii) the *pyrrolidin*-2-*one* **35** (36 mg, 55%) and the *pyrrol*-2-*one* **36** (6 mg, 9%) were eluted together. A small proportion of the *pyrrolidin*-2-*one* **35** was separated by HPLC (ethyl acetate–light petroleum, 2:5) as an oil; λ_{max}/nm 206 (ε/dm^3 mol^{-1} cm^{-1} 8700) and 237 (6550); ν_{max}/cm^{-1} 3100, 2975, 2940, 2880, 1690 (CO), 1665, 1495, 1455, 1310, 1250 and 930; δ_H(400 MHz) 5.96 [dd (*ca.* t), *J* 2.3 and 2.9, =C*H*H], 5.3 [dd, (*ca.* t), *J* 2.3 and 2.9, =CH*H*], 3.42 (t, *J* 6.6, ring-NCH$_2$), 3.38 (t, *J* 7.3, NCH$_2$), 2.75 [ddt (*ca.* tt), *J* 6.6, 2.9 and 2.6, =CCH$_2$], 1.55 (*ca.* quint., *J* 7.4, CH_2CH$_2$CH$_3$), 1.35 (*ca.* sextet, *J* 7.3, CH_2CH$_3$) and 0.95 (t, *J* 7.3, CH$_3$); δ_C(22.5 MHz) 167.6 (CO), 139.9 (=C), 114.4 (=CH$_2$), 43.8 (ring NCH$_2$), 42.6 (NCH$_2$), 29.0 (CH$_2$), 24.0 (CH$_2$), 19.8 (CH$_2$) and 13.4 (CH$_3$); *m/z* 153.1142 (28%) ($C_9H_{15}NO$ requires 153.1154), 138 (M − CH$_3$, 5), 124 (M − C_2H_5, 10), 110 (M − C_3H_7, 100) and 96 (M − C_4H_9, 7). The crude pyrrolone **36** displayed: δ_H(400 MHz) 6.65 [tq (*ca.* sextet), *J* 1.7 and 1.6, =CH], 3.8 [dq (*ca.* quint.), *J* 1.8 and 1.6, ring NCH$_2$], 3.45 (t, *J* 7.3, NCH$_2$), 1.9 [dt (*ca.* q), *J* 1.9 and 1.8, =CCH$_3$], 1.55 (*ca.* quint., *J* 7.5, CH_2CH$_2$CH$_3$), 1.35 (*ca.* sextet, *J* 7.3, CH_2CH$_3$) and 0.95 (t, *J* 7.3, CH$_2$CH_3).

(*b*) A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **33** (440 mg, 0.83 mmol) and pyridine (197 mg, 2.5 mmol) in dichloromethane (150 cm^3) was stirred and irradiated for 72 h and then subjected to the above isolation and purification procedures to give compounds **37** (8 mg, 6%), **35** (52 mg, 41%) and **36** (18 mg, 14%). The spectroscopic data for these compounds were identical with those obtained previously.

1-*Butyl*-3-(2,2,6,6-*tetramethylpiperidin*-1-*yloxymethyl*)*pyrrolidin*-2-*one* **38** *and* 2,2,6,6-*tetramethylpiperidin*-1-*yl*) N-(*But*-3-*enyl*)-N-*butylcarbamate* **39**.—A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **33** (91 mg, 0.17 mmol) and TEMPO **7** (27 mg, 0.17 mmol) in dichloromethane (30 cm^3) was stirred and irradiated under reflux in an atmosphere of nitrogen for 48 h. The resulting mixture was cooled and then evaporated

to dryness under reduced pressure to leave a brown solid. The solid was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:3) to yield: (i) the *carbamate* **39** (12 mg, 23%), was eluted first, as a pale yellow oil; ν_{max}/cm^{-1} 3080, 2960sh, 2930, 2860, 1730 (CO), 1640, 1470, 1415, 1380, 1365, 1210, 1145 and 760; δ_H(80 MHz) 6.0–5.55 (ddt, *J* 17.2, 9.8 and 6.5, =CH), 5.15–4.80 (m, $=CH_2$), 3.25 (t, *J* 6.7, NCH_2 allyl), 3.15 (t, *J* 5.3, NCH_2Pr), 2.3 [br dt (*ca.* br q), *J* 7.0 and 6.5, $=CHCH_2$], 1.8–0.8 [m, $(CH_2)_3$ and $CH_2CH_2CH_3$], 1.1 (2 × Me) and 1.0 (2 × Me); *m/z* 295.2384 (1%) ($C_{17}H_{31}N_2O_2$ requires 295.2386), 156 (TEMPO, 4), 154 (M − TEMPO, 50) and: (ii) the *pyrrolidin-2-one* **38** (31 mg, 59%), was eluted second, as a colourless oil; ν_{max}/cm^{-1} 3010, 2970sh, 2840, 2880, 1690 (CO), 1455, 1425, 1370, 1360 and 1265; δ_H(400 MHz) 4.1 (dd, *J* 8.5 and 4.9, OCHH), 3.9 (dd, *J* 8.5 and 3.4, OCHH), 3.4 (dt, *J* 8.4 and 6.0, ring NCHH), 3.35–3.2 (m, ring NCHH and NCH_2), 2.6 (br m, COCH), 2.25–2.05 (m, ring NCH_2CH_2), 1.55 (quint., *J* 7.4, $CH_2CH_2CH_3$), 1.6–1.3 [m, $(CH_2)_3$], 1.3 (sextet, *J* 7.3, CH_2CH_3), 1.2 (Me), 1.18 (Me), 1.1 (Me), 1.05 (Me) and 0.9 (t, *J* 7.3, CH_2CH_3); δ_C(100 MHz) 174.5 (CO), 75.6 (OCH_2), 60.1 (quat. C), 60.0 (quat. C), 46.1 (ring NCH_2), 42.5 (COCH), 42.4 (NCH_2), 39.7 (ring NCH_2CH_2), 39.6 (CH_2), 33.2 (CH_3), 32.8 (CH_3), 29.4 (CH_2), 22.2 (CH_2), 20.2 (CH_3), 20.1 (CH_2), 20.0 (CH_3), 17.0 (CH_2) and 13.8 (CH_3); *m/z* 310.2613 (8%) ($C_{18}H_{34}N_2O_2$ requires 310.2618), 295 (M − CH_3, 37), 156 (TEMPO, 44) and 154 (M − TEMPO, 39).

N-(2,2-*Dimethylpent-4-enyl*)-N-*propylamine* **41**.—A solution of concentrated hydrochloric acid (1.7 cm^3) in dry methanol (2.3 cm^3) was added dropwise over 1 min to a stirred solution of dry propylamine (3.55 g, 4.93 cm^3, 60 mmol) in dry methanol (19 cm^3) under an atmosphere of nitrogen. 2,2-Dimethylpent-4-enal (1.12 g, 10 mmol) was added dropwise to the mixture which was then stirred under an atmosphere of nitrogen for 1 h. Sodium cyanoborohydride (377 mg, 6 mmol) was added in one portion to the mixture which was then stirred under an atmosphere of nitrogen for 72 h and then cooled to 0 °C. Concentrated hydrochloric acid was added dropwise to the mixture until it attained pH 1 after which solvent was removed by evaporation under reduced pressure. Water (20 cm^3) was added to the residue and the resulting aqueous solution was then extracted with diethyl ether (3 × 20 cm^3). The remaining aqueous solution was cooled (0 °C) and brought to pH 10 by the slow addition of potassium hydroxide pellets. The liberated amine was extracted into diethyl ether (3 × 20 cm^3). The combined organic extracts were dried, filtered, and the solvent removed under reduced pressure to give a pale yellow liquid. This was further purified by Kugelröhr distillation to give the *amine* **41** (1.13 g, 73%) as a colourless liquid, b.p. 120 °C/25 Torr; ν_{max}/cm^{-1} 3080, 2970, 2940, 2880, 2820, 1660, 1640, 1465, 1385, 1370, 1130 and 920; δ_H(80 MHz) 6.05–5.5 (ddt, *J* 17.9, 8.9 and 7.3, =CH), 5.1–4.85 (br m, $=CH_2$), 2.5 (t, *J* 7.3, NCH_2Et), 2.3 (NCH_2CMe_2), 2.0 (d, *J* 7.3, $=CHCH_2$), 1.7–1.2 (*ca.* sextet, *J* 7.0, CH_2CH_3), 0.9 (NH), 0.85 (t, *J* 7.0, CH_2CH_3) and 0.85 (2 × Me); δ_C(20 MHz) 135.4 (=CH), 116.5 ($=CH_2$), 60.2 (NCH_2), 52.8 (NCH_2), 44.7 (CH_2), 34.1 (CMe_2), 25.4 (CH_3), 23.0 (CH_2) and 11.5 (CH_3); *m/z* 155 (M, 1%), 154 (M − H, 2), 140 (M − CH_3, 7), 126 (M − C_2H_5, 10), 112 (M − C_3H_7, 3) and 72 (M − C_6H_{11}, 100) (Found: C, 77.65; H, 13.75; N, 9.15%; M, 155.1671. $C_{10}H_{21}N$ requires C, 77.35; H, 13.65; N, 9.0%; *M*, 155.1674).

N-(2,2-*Dimethylpent-4-enyl*)-N-*propylcarbamoyl Chloride* **42**.—A solution of the amine **41** (655 mg, 4.22 mmol) in dry benzene (3 cm^3) was added dropwise over 0.5 min to a stirred suspension of dry pyridine (334 mg, 4.22 mmol) and triphosgene (417 mg, 1.41 mmol) in dry benzene (30 cm^3) under an atmosphere of nitrogen. The resulting suspension was stirred under nitrogen for 72 h, and then filtered under nitrogen. The filtrate was evaporated to dryness under reduced pressure to leave the *carbamoyl chloride* **42** (900 mg, 98%) as a yellow liquid; ν_{max}/cm^{-1} 3085, 3060, 2980, 2950, 2790, 1740 (CO), 1640, 1605, 1470, 1405, 1210, 1105, 935, 735 and 700; δ_H(80 MHz) 6.15–5.55 (ddt, *J* 15.3, 11.5 and 7.3, =CH), 5.12 (br d, *J* 11.5, =CHH), 5.09 (br d, *J* 15.3, =CHH), 3.4 (t, *J* 7.5, NCH_2Et), 3.25 (NCH_2CMe_2), 2.05 (d, *J* 7.3, $=CHCH_2$), 2.0–1.45 (*ca.* sextet, *J* 7.5, CH_2CH_3), 0.95 (2 × Me) and 0.9 (t, *J* 7.5, CH_2CH_3); *m/z* 219 [M (^{37}Cl), 0.44%], 217 [M (^{35}Cl), 1.12] and 182 (M − Cl, 11).

N-(2,2-*Dimethylpent-4-enyl*)-N-*propylcarbamoyl*(*salophen*)-*cobalt*(III) **43**.—A deoxygenated solution of the carbamoyl chloride **42** (900 mg, 4.15 mmol) in dry THF (10 cm^3) was injected during 1 min into a stirred green solution of sodium (salophen)cobaltate(I) **2** (4.6 mmol) in dry, deoxygenated THF (200 cm^3) in the dark under an atmosphere of argon. The resulting brown solution was stirred for 1 h then filtered under reduced pressure. The filtrate was evaporated to dryness under reduced pressure in the dark at room temperature to leave a red–brown solid residue. The residue was pre-adsorbed onto Woelm alumina and purified by column chromatography over Woelm alumina (diethyl ether→methanol–dichloromethane, 1:100) to give the *title compound* **43** (1.01 g, 44%) as a deep red crystalline solid, m.p. > 100 °C (decomp.); λ_{max}/nm 199 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 40 000), 229 (29 400), 257 (30 000), 302 (17 000) and 367 (11 900); ν_{max}/cm^{-1} 3140, 2940, 2880, 1635sh (CO), 1610, 1580, 1460, 1435, 1335, 1155 and 1085; δ_H(80 MHz) 8.7 (2 × HC=N), 8.0 (m, 2 × ArH), 7.5–7.1 (m, 8 × ArH), 6.9–6.6 (m, 2 × ArH), 5.75–5.10 (m, =CH), 4.9–4.5 (m, $=CH_2$), 4.2–3.8 (br m, NCH_2Et), 3.1 (br s, NCH_2CMe_2), 1.8–1.2 (m, $=CHCH_2$ and CH_2CH_3), 0.9 (t, *J* 7.6, CH_2CH_3) and 0.35 (2 × Me); *m/z* (FAB) 555 (M, 7%), 374 [Co(salophen) + H, 25] and 181 [M − Co(salophen), 4].

5,5-*Dimethyl-3-methylene-1-propylpiperidin-2-one* **49**, 3,5,5-*Trimethyl-1-propyl-5,6-dihydropyridin-2-one* **50**, 5,5-*Dimethyl-1-propyl-5,6,7,8-tetrahydroazepin-2-one* **51** *and* N-(2,2-*Dimethylpent-4-enyl*)-N-*propylformamide* **45**.—(*a*) A deoxygenated solution of the carbamoyl(salophen)cobalt(III) **43** (350 mg, 0.63 mmol) in freshly distilled dry toluene (40 cm^3) was stirred and heated under reflux in an atmosphere of nitrogen for 48 h. The resulting mixture was cooled and then evaporated to dryness under reduced pressure to leave a brown solid residue. The solid was pre-adsorbed onto silica gel and purified by column chromatography over silica gel (diethyl ether–light petroleum, 1:3) to yield: (i) the dihydropyridin-2-one **50** (8 mg, 7%), eluted first, as a pale yellow oil; λ_{max}/nm 206 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 9450) and 249 (2650); ν_{max}/cm^{-1} 2940, 2870, 1670sh (CO), 1615 (C=C), 1480, 1380, 1360 and 1310; δ_H(80 MHz) 6.0 (br q, *J* 1.2, =CH), 3.35 (t, *J* 7.2, NCH_2Et), 3.1 (br s, ring-CH_2), 1.85 (d, *J* 1.2, $=CCH_3$), 1.8–1.3 (*ca.* sextet, *J* 7.4, CH_2CH_3), 1.05 (2 × Me) and 0.9 (t, *J* 7.2, CH_2CH_3); *m/z* 181 (M, 29%), 166 (M − CH_3, 15), 152 (M − C_2H_5, 100), and: (ii) the *formamide* **45** (< 1 mg), eluted second, as a colourless oil; ν_{max}/cm^{-1} 2940, 2880, 1665 (CO), 1660, 1465, 1400, 1110 and 925; δ_H(80 MHz) 8.15 and 8.0 (1 H, each s, CHO), 6.10–5.55 (m, =CH), 5.15–4.90 (br m, $=CH_2$), 3.3 and 3.2 (2 H, each t, *J* 7.3, NCH_2Et), 3.1 and 3.0 (2 H, each s, NCH_2CMe_2), 2.0 (dd, *J* 7.4 and 1.2, $=CHCH_2$), 1.8–1.3 (sextet, *J* 7.3, CH_2CH_3), 0.95 (2 × Me) and 0.9 (t, *J* 7.4, CH_2CH_3); *m/z* 183.1619 (6%) ($C_{11}H_{21}NO$ requires 183.1623), 154 (M − C_2H_5, 24), 142 (M − C_3H_5, 11), 100 (M − C_6H_{11}, 100), and: (iii) the *piperidin-2-one* **49** (58 mg, 51%), eluted third, as a colourless oil; λ_{max}/nm 213 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 11 450) and 242 (4750); ν_{max}/cm^{-1} 2980, 2940, 2890, 1665 (CO), 1620 (C=C), 1490, 1470, 1300, 1200, 940 and 810; δ_H(400 MHz) 6.25

(d, J 1.6, =CHH), 5.25 (d, J 1.6, =CHH), 3.35 [dd (*ca.* t), J 7.5, NCH_2Et], 3.1 (NCH_2CMe$_2$), 2.35 (br s, =CCH$_2$), 1.65–1.55 (*ca.* sextet, J 7.5, CH_2CH$_3$), 1.02 (2 × Me) and 0.92 (t, J 7.4, CH$_2$CH_3); δ_C(100 MHz) 163.7 (CO), 136.6 (=C), 122.6 (=CH$_2$), 60.2 (NCH$_2$CMe$_2$), 49.3 (NCH$_2$), 43.6 (=CCH$_2$), 30.4 (CMe$_2$), 26.0 (CH$_3$), 20.2 (CH$_2$) and 11.4 (CH$_3$); m/z 181.1447 (49%) ($C_{11}H_{19}NO$ requires 181.1467), 166 (M − CH$_3$, 26), 152 (M − C_2H_5, 100), and: (iv) the *tetrahydroazepin-2-one* **51** (8 mg, 7%), eluted fourth, as a colourless oil; λ_{max}/nm 208 (ε/dm^3 mol^{-1} cm^{-1} 11 000) and 239 (4400); ν_{max}/cm^{-1} 2940, 2880, 1645 (CO), 1600 (C=C), 1470, 1430, 1390, 1375 and 1175; δ_H(400 MHz) 6.25 (dt, J 11.3 and 6.4, HC=CHCO), 6.00 (d, J 11.3, COCH=), 3.41 [dd (*ca.* t), J 7.7, NCH_2Et], 3.00 (NCH_2CMe$_2$), 2.01 (d, J 6.4, =CHCH_2), 1.65–1.55 (*ca.* sextet, J 7.6, CH_2CH$_3$), 1.0 (2 × Me) and 0.9 (t, J 7.4, CH$_2$CH_3); δ_C(100 MHz) 169.6 (CO), 136.8 (HC=CHCO), 128.5 (=CHCO), 58.6 (NCH$_2$-CMe$_2$), 50.8 (NCH$_2$Et), 41.0 (CMe$_2$), 39.8 (=CHCH$_2$), 27.2 (CH$_3$), 21.3 (CH$_2$) and 11.5 (CH$_3$); m/z 181.1465 (24%) ($C_{11}H_{19}NO$ requires 181.1467), 166 (M −CH$_3$, 14), 152 (M − C_2H_5, 57) and 138 (M − C_3H_7, 10).

(*b*) A deoxygenated solution of the carbamoyl(salophen)-cobalt(III) **43** (340 mg, 0.61 mmol) and pyridine (0.15 g, 0.15 cm^3, 1.8 mmol) in dichloromethane (150 cm^3) was stirred and irradiated under reflux under an atmosphere of nitrogen for 72 h. Isolation and purification of the products as described above gave **50** (10 mg, 9%), **45** (2.5 mg, 2%), **49** (36 mg, 32%), and **51** (trace). The spectroscopic data for these compounds were identical with those obtained previously.

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