Selective Functionalisation. Part 11. Selective Hydrogenation by a Novel Palladium Salicylidene-ethylenediamine Complex and the Properties of Derivatives of some Square Planar Homogeneous Hydrogenation Catalysts

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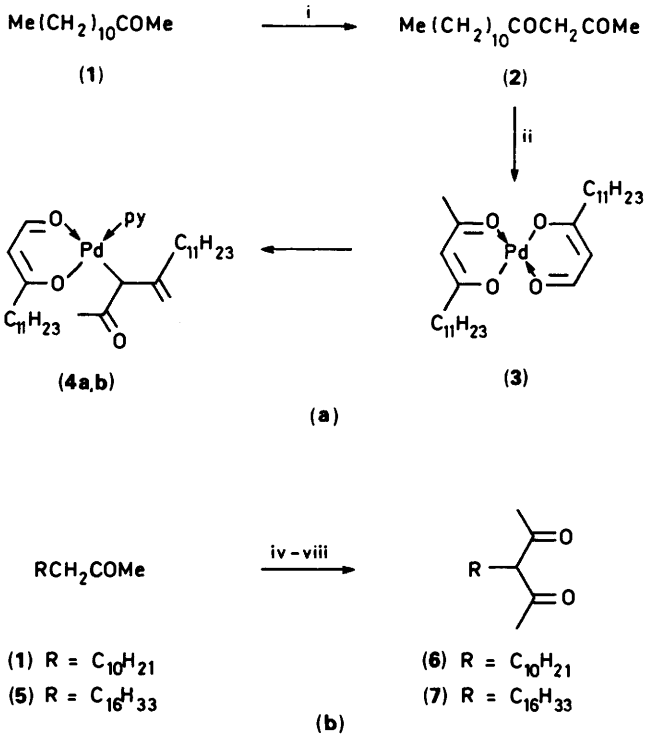
Analogues of two reported homogeneous hydrogenation catalysts based upon square planar palladium complexes have been prepared with a view to modifying the structures to permit the control of selectivity by micellar interactions. Derivatives of bisacetylacetonatopalladium(II) in which the diketone was alkylated at C-3 or C-5 were prepared but no useful catalytic activity was observed for the reduction of nitrobenzene to aniline in the presence of pyridine. Complexes were also prepared from bisacetylacetonatopalladium(II) with 4-substituted pyridines as ligands; 4-tridecylpyridine afforded an unstable complex but 4-decylaminopyridine afforded a stable complex with low catalytic activity. A series of salicylidene imine palladium(II) complexes was prepared. Contrary to previous reports, the well-known salicyclidene-ethylenediaminepalladium(II) complex was not a catalyst for homogeneous hydrogenation but a new oligomeric green heterogenous complex with selective hydrogenation properties was discovered. This green complex was selective for the hydrogenation of alkynes, especially terminal alkynes, and reduced few other functional groups ($ArNO_2$, ArCHO). Many variations on this structure were investigated in an attempt to discover a soluble or crystalline analogue of the green complex but no complexes with improved properties were isolated.

In our work on selective functionalisation we have studied the effects of several types of molecular interaction to control selectivity in the functionalisation of small aromatic molecules. Most recently, donor-acceptor interactions and hydrogen bonds have been successfully used to control the nitration of phenol[1] but this work arose from a study of the micellar chlorination[2] and hydroxylation[3] of monosubstituted benzene derivatives. Because the yields in the latter reactions were low, despite interesting selectivity, we wished to modify our systems to study potentially high yielding reactions such as hydrogenation. Of the homogeneous catalytic systems described in the literature, two seemed particularly suited to an extension of our previous work because, as in our studies, they were built from bidentate or tetradentate ligands, namely bisacetylacetonatopalladium(II)[4] and salicylidene-ethylenediaminepalladium(II).[5–8] The latter, in particular, was related to the 2-hydroxybenzylamine ligands used in our previous work.[3] We have therefore prepared a series of analogues of the prototype systems described in the literature and investigated their properties as hydrogenation catalysts. The principal discovery of the programme was the identification of a new type of palladium complex that is a selective heterogeneous hydrogenation catalyst.

Results and Discussion

Analogues of Bisacetylacetonatopalladium(II).—Three points of modification of the prototype structure[4] were investigated. Firstly the length of the acetylacetone chain was extended by the preparation of pentadecane-2,3-dione complexes [Scheme 1a; (**4a, b**)], and secondly, branched chain diketones (**6**) and (**7**) were prepared (Scheme 1b). Complexes were obtained with (**4a, b**) but (**6**) and (**7**) failed to form complexes with palladium in the presence of weak bases such as ammonia, triethylamine, and sodium acetate using potassium tetrachloropalladate or bisbenzonitriledichloropalladium as sources of the metal; the ligand was recovered unchanged. When a stronger base, sodium hydroxide, was used, decomposition of the ligand occurred. Finally, long alkyl groups were inserted at the 4-position of the pyridine ligand required for catalytic activity[4] (Scheme 1c). 4-Tridecylpyridine (**8**) was treated with bisacetylacetonatopalladium to form an isolable complex (**9**); because of the limited catalytic activity of this complex (see below), it was only partially characterised. The second pyridine derivative was 4-decylaminopyridine (**10**) which formed a palladium complex (**11**) that was well characterised.

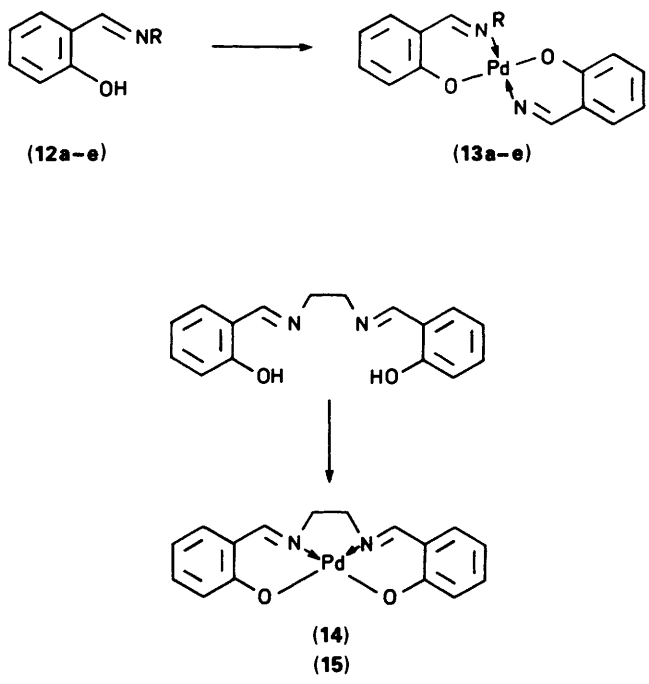
Each of the isolated complexes was studied for its catalytic properties using the reduction of nitrobenzene as a test reaction; this reaction was found to occur easily with the prototype system.[4] The chief problem encountered was decomposition of the complexes leaving black residues that probably contained metallic palladium whence some catalytic activity arose. Complexes (**4a, b**), used as a mixture, decomposed in non-polar solvents such as light petroleum (b.p. 100–120 °C). Although soluble in ethanol and in micellar solutions of hexadecylpyridinium chloride, sodium dodecyl sulphate, and polyoxyethylene(6)dodecanol, no reduction of nitrobenzene was observed under these conditions. More success was obtained with the pyridine derivatives: the 4-tridecylpyridine complex (**9**) achieved some hydrogenation (50%) before decomposition with light petroleum or ethanol as solvents. The 4-decylaminopyridine complex (**11**) formed a stable complex that had weak catalytic activity; only 18% reduction of nitrobenzene was observed in 24 h but no decomposition was detected. The principal conclusion to be drawn from these experiments is that simple homogeneous catalysts are structurally extremely sensitive in their requirements for activity and the direct modification of a catalyst to



Scheme 1. *Reagents:* i, NaH, EtOAc; ii, K_2PdCl_4; iii, py; iv, Ac_2O; v, H^+; vi, BF_3/Ac_2O; vii, BF_3; viii, H_3O^+; ix, PhLi, $C_{12}H_{25}Br$; x, $[Pd(acac)_2]$; xi, $C_9H_{17}COCl$, Et_3N; xii, $LiAlH_4$.

change its selectivity appears to be very much a matter of chance.

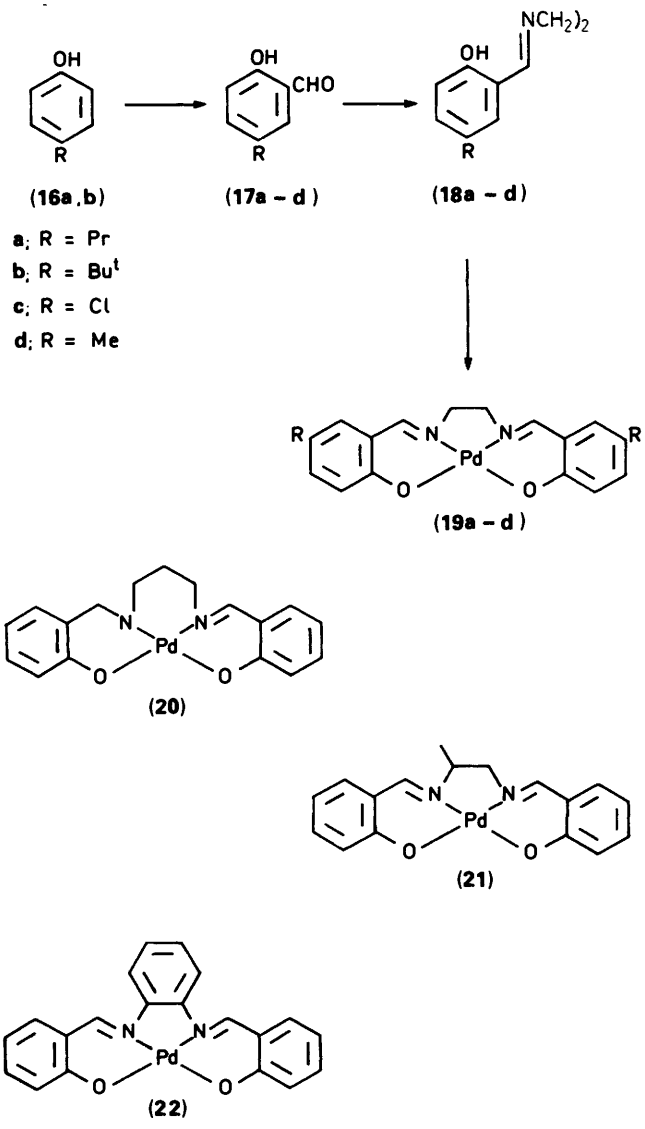
Complexes of Salicylideneethylenediamine.—Several authors have described the ability of palladium salen complexes to act as homogeneous hydrogenation catalysts.[5–8] Our initial experiments were a direct extrapolation of our previous work; a series of palladium complexes (**13a–e**) was prepared from readily available salicylaldimines (Scheme 2). These yellow diamagnetic complexes were carefully purified and tested as hydrogenation catalysts. However no reduction was obtained. The same result attended the use of purified palladium salen



Scheme 2.

itself as catalyst, despite reports to the contrary.[5–8] Since some of the reported work did not purify the complex but used it *in situ*, it was possible that an impurity might be a catalytically active species. Indeed when we prepared the complex using Baryshnikov's method[8] using triethylamine as the base, we observed that a pale green colouration developed. This colour was lost on purification of the Pd(salen) complex (**14**) but, equally, the product was catalytically inactive. It was possible to isolate the green material by washing the crude product of the reaction with warm dimethylformamide; the yellow inactive complex was soluble and the novel green material (**15**) was filtered off. Elemental analysis showed this material to be essentially a 1:1 palladium ligand complex but a small proportion of chlorine always remained. As discussed below, we formulate this product as an oligomer of Pd(salen) on the basis of physical and chemical data including the fact that the green product is slowly converted into the monomeric yellow complex on warming in a suitable solvent. Complete characterisation of the product, however, was not achieved and in view of its significant catalytic activity, we attempted the preparation of analogues that might have enhanced solubility or crystallisation properties.

Attempts to improve solubility were made by introducing alkyl groups into the benzene rings (Scheme 3); both the 4,4′-propyl and 4,4′-t-butyl compounds were prepared. A yellow monomeric complex could, in each case, be isolated (**19a, b**) and a black, insoluble residue was obtained also. Neither of these residues lent themselves to isolation and purification; elemental analysis showed that they had very low C, H, and N content and that there was always some residual chlorine. Unlike the parent compound of the series (**15**), neither of these by-products was converted into the yellow major monomeric product when heated. To improve crystallinity, smaller substituents, chloro (**19c**) and methyl (**19d**) were introduced. Both of these ligands afforded green compounds and yellow compounds but the former did not lend themselves to isolation decomposing to black residues at temperatures as low as that of refluxing dichloromethane. Further bidentate ligands with methyl and phenyl substituents (**13a, e**) were investigated but, as with the previous molecules of this series, no trace of green compound



Scheme 3.

was formed. Finally, complexes formed from alternative diamines, propane-1,3-diamine (**20**), propane-1,2-diamine (**21**), and *o*-phenylenediamine (**22**) were prepared. Of these, only the first showed the formation of even a trace of green product; the others afforded no trace of an isomeric product.

Characterisation of the Novel Green Complex (**15**).—As mentioned above, elemental analysis on the insoluble green compound (**15**) established that it was essentially a 1:1 complex of ligand and metal although some chlorine (~1%) was always present. The mass spectra of the green complexes and yellow complexes likewise showed the same molecular ion (372 for Pd^{106}). The IR spectra indicated that the green complex (**15**) was less symmetrical than the yellow complex (**14**); whereas (**14**) showed bands at 1627 and 1595 cm^{-1} corresponding to the imine and benzene ring respectively, (**15**) showed a broader band with a maximum at 1620 cm^{-1} and shoulders at 1625, 1615, and 1595 cm^{-1}. The fingerprint regions of the spectra were also completely different. ^{13}C NMR spectra of the complexes confirmed the lack of symmetry of (**15**). The spectrum of (**14**) showed resonances at 157.9 and 121.5 ppm for the imine carbon and the quaternary carbon of the benzene ring whereas the green complex (**15**) showed double the number of resonances namely 167.5 and 164.1 for the imine carbons, and

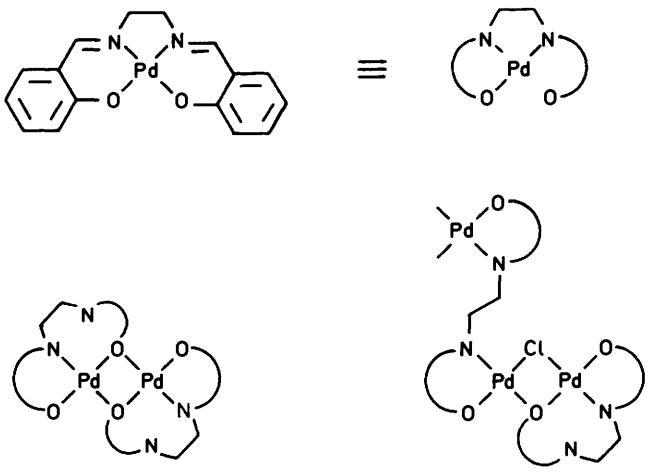


Figure 1. Possible structures for the green complex (**15**) based upon analytical and spectroscopic data and literature precedent.[9]

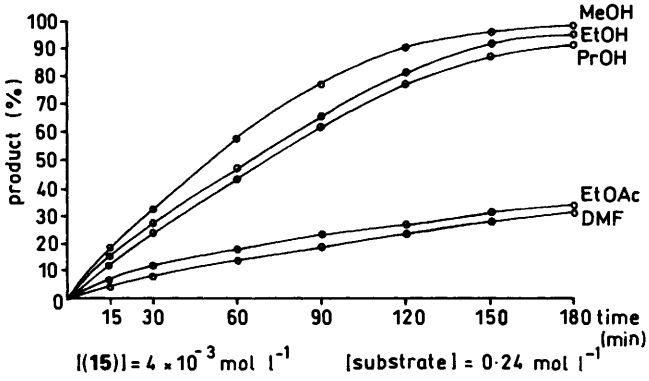


Figure 2. Hydrogenation of cyclohexene over a 3 h reaction period using complex (**15**) suspended in various solvents.

120.9 and 119.2 ppm for the quaternary carbon. The available data is insufficient to define a unique structure for (**15**) but the chemical reactivity and the insolubility suggest that the compound may be an oligomer of Pd(salen) in which the ligands act as bridging groups between two palladium atoms. The residual chlorine could then be assigned to terminal sites that end the oligomeric chain. Figure 1 shows some possibilities for which there is precedent in nickel complexes.[9] Assuming that two chlorine atoms act as end groups, it is possible to estimate that approximately 10 salen ligands contribute to the oligomer from the elemental analysis data. Whatever structure proves to be correct, it is notable that the palladium atoms in (**15**) would be expected to be more susceptible to ligand exchange in these structures than in the yellow complex (**14**), a factor that is probably related to the catalytic activity of the green material.

Catalytic Activity of the Green Complex (**15**).—The first parameter to be investigated in the evaluation of the new catalyst was the effect of *solvent* so that the optimum conditions could be defined for more detailed studies of structure–activity relationships in substrates. Cyclohexene was chosen as the test substrate and the results are shown in Figure 2 for a 60:1 substrate:catalyst ratio. Alcohols proved to be most favourable solvents; strongly donating solvents such as pyridine or dimethylformamide inhibited hydrogenation.

Structure–Activity Relationships in Alkene Hydrogenation.—The Table reports the results obtained for the hydrogenation of an extensive series of simple alkenes in methanol solution.

Table. Hydrogenation of representative alkenes using compound (**15**) suspended in methanol.

Substrate	[Substrate] / mol l^{-1}	[(**28b**)] / mol l^{-1}	Ratio Substrate: Catalyst	Reaction time	Result (yield %)
(i) $PhCH{=}CH_2$	0.27	8.95×10^{-4}	300:1	19 min	$PhCH_2Me$ (100)
(ii) $CH_2{=}CH(CH_2)_3Me$	0.27	8.95×10^{-4}	300:1	5 min	$Me(CH_2)_4Me$ (11.1)
(iii) $CH_2{=}CH(CH_2)_3Me$	0.27	8.95×10^{-4}	300:1	50 min	$CH_2{=}CH(CH_2)_3Me$ (14) $Me(CH_2)_4Me$ (42) $MeCH{=}CH(CH_2)Me$ (44)
(iv) $CH_3CH{=}CH(CH_2)_2Me$	0.27	8.95×10^{-4}	300:1	50 min	$Me(CH_2)_4Me$ (3)
(v) $\overline{CH_2(CH_2)_3CH{=}CH}$	0.24	4.0×10^{-3}	60:1	3 h	$\overline{CH_2(CH_2)_4CH_2}$ (>99)
(vi) $\overline{CH_2(CH_2)_3CH{=}CHMe}$	0.24	4.0×10^{-3}	60:1	9 h	$\overline{CH_2(CH_2)_4CHMe}$ (6)
(vii) $Me_2\overline{CCH_2C(O)CH{=}C(Me)CH_2}$	0.24	4.0×10^{-3}	60:1	9 h	$Me_2\overline{CCH_2C(O)CH_2CH(Me)CH_2}$ (16)
(viii) $MeCH{=}CMe_2$	0.24	4.0×10^{-3}	60:1	9 h	$MeCH_2CHMe_2$ (2)
(ix) $HO_2CCH{=}CHCO_2H$	0.24	4.0×10^{-3}	60:1	4 h	$HO_2CCH_2CH_2CO_2H$ (100)
(x) $HO_2CCH{=}CHCO_2H$	0.24	4.0×10^{-3}	60:1	4 h	$HO_2CCH_2CH_2CO_2H$ (100)

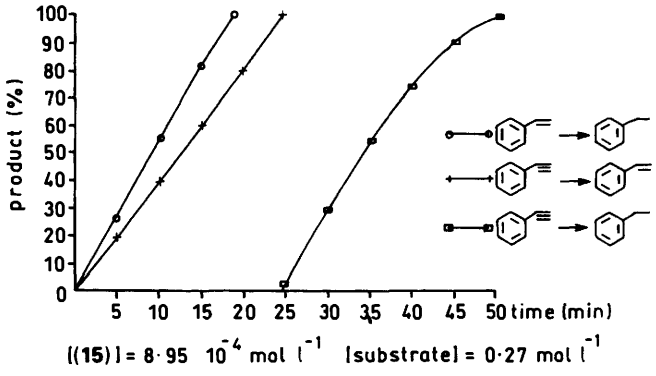


Figure 3. Hydrogenation of phenylacetylene and styrene using complex (**15**) suspended in methanol.

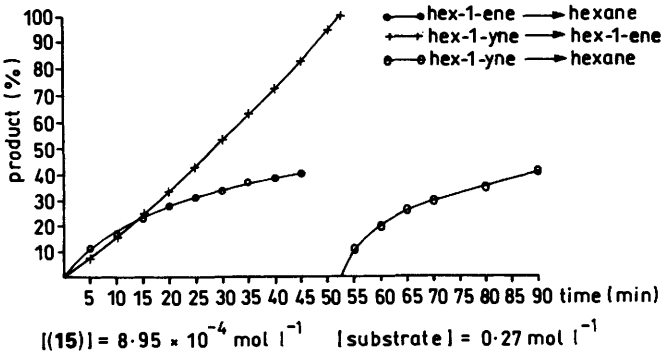


Figure 4. Hydrogenation of hex-1-yne and hex-1-ene using complex (**15**) suspended in solvent methanol.

The following trends were discernible. (1) Steric hindrance to hydrogenation was marked in both cyclic and acyclic alkenes. (2) Initial rate measurements showed that terminal acyclic alkenes reacted *ca.* 110 times faster than internal acyclic alkenes, a result qualitatively similar to the behaviour of $[RuCl_2PPh_3]$[10] and $[RhCl(PPh_3)_3]$.[11] (3) Double bond migration reduces the overall rate of hydrogenation of terminal alkenes. (4) α,β-Unsaturated alkenes were somewhat activated with respect to a similar alkyl substituted alkene.

Alkyne Hydrogenation.—The inhibition of alkene reduction by donor solvents such as pyridine led us to wonder whether it was possible to effect a clean sequential hydrogenation of alkyne to alkene without significant further reduction to the alkane. We found that stepwise reduction was indeed possible and Figures 3 and 4 display some of the relevant data. It was interesting, however, that the selectivity was evidently not due to the more rapid rate of hydrogenation of alkynes. Indeed, for the two examples quoted, phenylacetylene and hex-1-yne, the alkyne underwent hydrogenation some 27 and 35% respectively slower than the corresponding alkene as measured by initial rates in separate experiments for alkyne and alkene. However in both cases, the hydrogenation of the alkyne was greater than 98% selective. This high selectivity for alkynes is unusual for a heterogeneous catalyst and is similar in this respect to that of $[RhCl(PPh_3)_3]$.[10] Alkene reduction can also be further inhibited by use of the pyridine as solvent; pyridine presumably competes successfully for the active palladium sites with the alkene. On the other hand, alkynes, which are better donors than alkenes, undergo steady reduction. From experiments on internal alkynes (diethyl acetylenedicarboxylate, 3-hexyn-1-ol, and phenylpropynoic acid), the stereochemistry of alkyne reduction was shown to favour the *cis*-alkene product. Only in the last case was a mixture formed after uptake of 1 equiv. of hydrogen; the product was composed of 90% *cis* and 10% *trans* isomers.

Reduction of Other Functional Groups.—Apart from alkenes and alkynes, few functional groups were found to be reduced by the green salen complex (**15**) at atmospheric pressure. The most successful reactions were with nitrobenezene and benzaldehyde, in which quantitative reduction was observed, although limited hydrogenolysis of benzyl acetate occurred. Dibenzyl ether was cleaved to the extent of 3% in the time taken to reduce nitrobenzene completely. No reaction was observed with 2-nitropropane, propanal, cyclohexanone, acetophenone, ethyl acetate, benzyl alcohol, iodobenzene, or cyclopropylbenzene. In these respects and in the selectivity of reduction of alkynes, the green salen complex (**15**) shows different selectivity from that of the conventional heterogeneous catalyst, palladium on charcoal.

Recovery of Catalyst and Its Re-use.—Palladium on charcoal is a recoverable and re-usable catalyst. It was important to investigate the potential of the new heterogeneous catalyst (**15**) for recovery and re-use. Accordingly a series of three consecutive hydrogenations of hept-1-yne was carried out using

the same batch of catalyst. After each reaction, the catalyst was filtered off, washed, and dried, and then submitted for elemental analysis and spectroscopic examination. With regard to the progress of the reaction, the rate and selectivity of hydrogenation was found to be identical for each run. The recovered catalyst material was also indistinguishable from freshly prepared complex by IR and mass spectrometry. Some change in elemental composition was observed in a reduction of the proportions of carbon, hydrogen, and nitrogen, and an increase in the proportion of chlorine. This result taken with the observation that the washings from the catalyst contained yellow monomer (**14**) together with free salen ligand identified by TLC suggested that a small proportion of the green catalyst was reverting to the more stable yellow monomer. Undoubtedly, part of this change took place in the washing procedure and the decomposition of the green catalyst can be estimated to be not greater than 3.5% per run. The increase in chlorine content can be explained by a reduction in the number of units in the oligomer of the green complex and a corresponding increase in the proportion of chlorine end groups.

Conclusions.—It is clear from the above work that small changes in the structure of homogeneous catalysts can lead to a substantial deterioration in their performance and that the design of catalysts to have defined specificity is not a simple matter. Equally, the importance of proper characterisation of materials used in catalytic studies is emphasised. Most importantly, however, the discovery of a new type of catalyst, the green complex (**15**) suggests new opportunites for both catalytic and structural research.

Experimental

Pentadecane-2,4-dione (**2**).[12]—Ethyl acetate (2.66 g, 30 mmol) was added to a stirred suspension of sodium hydride (60% w/w; 0.697 g, 0.0174 mol, 15% excess) in dry ether (25 ml) under nitrogen. These contents were heated gently under reflux whilst a solution of tridecan-2-one (3.00 g, 0.015 mol) in dry ether was added dropwise over 45 min. This solution was than stirred and heated under reflux for 12 h, before it was cooled to room temperature and dilute hydrochloric acid (1M; 16 ml) in crushed ice (60 g) was added. Stirring was continued until all the solids had dissolved. The solution was then transferred to a separating funnel and the ether layer removed. The aqueous layer was extracted once with ether (30 ml) and the combined ether extracts were washed with 5% aqueous sodium hydrogen carbonate (40 ml) and evaporated to dryness to yield a crude liquid (2.81 g).

This liquid was dissolved in warm ethanol (25 ml) and to this stirred solution was added a hot filtered solution of copper acetate monohydrate (1.52 g, 0.0076 mol) in water (20 ml). This solution was stirred for 30 min before the resulting precipitate was collected and air dried on a Büchner filter funnel. It was then washed with light petroleum (b.p. 40–60 °C; 3 × 30 ml) before it was transferred to a separating funnel and shaken with a mixture of 10% sulphuric acid (30 ml) and ether (40 ml) until all the solids had dissolved. The ether layer was removed and the aqueous layer extracted with ether (30 ml). The combined ether extracts were then washed with 5% aqueous sodium hydrogen carbonate (40 ml) and water (40 ml). Finally, the ether extracts were dried (K_2CO_3) and evaporated to dryness to give a liquid which on distillation (0.2 mmHg, 195–205 °C) yielded the title compound (2.57 g, 71%) as a clear solid, m.p. 31 °C (Found: 75.3; H, 12.05. Calc. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%); λ_{max}(EtOH) 275 nm (ε 4 800 dm^3 mol^{-1} cm^{-1}); ν_{max}(liquid film) 3 470br (enolic OH), 2 955, 2 925, and 2 850 (CH), 1 700 (C=O), and 1 610 cm^{-1} (enolic C=O); δ_H(90 MHz, $CDCl_3$), 0.90 (3 H, t, CH_3), 1.29–2.60 [20 H, m, $CO(CH_2)_{10}$], 2.05 (3 H, s, CH_3CO), 3.56 (2 H, s, $COCH_2CO$), and 5.49 (1 H, s, C=CH).

[*Bis*(*pentadecane-2,4-dionato*)]*palladium*(II) (**3**).—Palladium dichloride (0.114 g, 6.43 × 10^{-4} mol) was dissolved in a warm (*ca.* 65 °C) solution of ethanol (30 ml) and 1M aqueous potassium chloride (30 ml). This solution was allowed to cool to room temperature before it was added to a stirred solution of pentadecane-2,4-dione (0.338 g, 1.41 × 10^{-3} mol) in a mixture of ethanol (15 ml) and water (15 ml). This mixture was then stirred for 2 h, after which time the resulting precipitate was filtered off and recrystallised twice from a benzene–ethanol to give pale yellow crystals of compound (**9**) (0.180 g, 48%), m.p. 108–109 °C (Found: C, 61.55; H, 9.4. Calc. for $C_{30}H_{54}PdO_4$: C, 61.58; H, 9.30%); λ_{max}(cyclohexane) 215 (ε 26 800 dm^3 mol^{-1} cm^{-1}), 231 (29 600), and 330 nm (11 400) ν_{max}(KCl) 2 960, 2 920, and 2 850 (CH), and 1 565 cm^{-1} (C–O); δ_H(90 MHz, $CDCl_3$) 0.90 (6 H, t, CH_3), 1.30–2.00 [36 H, m, $COCH_2(CH_2)_9$], 2.08 (6 H, s, $COCH_3$), 2.30 (4 H, t, $COCH_2$), and 5.40 (2 H, s, CH).

[*Mono*(*pyridine*)*bis*(*pentadecane-2,4-dionato*)]*palladium*(II) (**4a, b**).—[Bis(pentadecane-2,4-dionato)]palladium(II) (**3**) (0.170 g, 2.91 × 10^{-4} mol) and pyridine (3 ml) were heated gently on a steam-bath for 20 min or until all of compound (**9**) had dissolved. This solution was then stirred at room temperature for a further 2 h before pyridine was distilled off [0.1 mmHg, maximum temp. (45 °C)] to give compound (**10**) as a yellow solid; ν_{max} 2 950, 2 920, and 2 840 (CH), 1 680 plus 1 640 (C=O of carbon bonded pentadecane-2,4-dionate ligand) and 1 565 plus 1 540 cm^{-1} (C=O and C=C respectively of oxygen bonded pentadecane-2,4-dionate ligand); δ_H(90 MHz, $CDCl_3$) 0.89 (6 H, t, CH_3), 1.26–2.56 [40 H, m, $CO(CH_2)_{10}$], 1.91 plus 2.02 [3 H, two singlets, $COCH_3$ *cis* (**10a**) and *trans* (**10b**) respectively to the pyridine ligand of the pentadecane-2,4-dionate ligand that is oxygen bonded to palladium], 2.18 (3 H, s, $COCH_3$ of pentadecane-2,4-dionato ligand that is carbon bonded to palladium), 4.27 plus 4.31 (1 H, two singlets, methine proton of carbon-palladium bonded ligand), 5.37 plus 5.38 (1 H, two singlets, methine proton of oxygen-palladium bonded ligand), 7.37 (2 H, t, pyr.), 7.78 (1 H, t, pyr.), and 8.74 (2 H, d, pyr.).

3-*Decylpentane*-2,4-*dione* (**6**).[13]—Tridecan-2-one (3.00 g, 0.015 mol), acetic anhydride (3.52 g, 0.0345 mol), and toluene-*p*-sulphonic acid monohydrate (0.116 g, 6.1 × 10^{-4} mol) were stirred at room temperature for 30 min. A solid 1:1 boron trifluoride–acetic acid complex (3.84 g, 0.03 mol) was then added and the resulting mixture stirred in a sealed flask for 20 h. A solution of sodium acetate trihydrate (8.78 g, 0.064 mol) dissolved in water (50 ml) was then added and contents refluxed for 3 h. After the solution had cooled to room temperature it was transferred to a separating funnel and the organic products extracted with ether (3 × 30 ml). The combined ether extracts were washed with 5% aqueous sodium hydrogen carbonate (2 × 30 ml) and saturated brine (2 × 30 ml). The ether layer was then dried ($MgSO_4$) and evaporated to dryness to give a crude liquid product (2.95 g). This crude product was purified *via* copper complex formation. This involved dissolving the crude product in warm ethanol (25 ml) and adding to this stirred solution, a hot filtered solution of copper acetate monohydrate (1.70 g, 0.0085 mol) in water (20 ml). This solution was stirred for 1 h before the resulting precipitate was collected and air dried on a Büchner filter funnel. It was then washed with light petroleum (b.p. 40–60 °C; 3 × 30 ml), transferred into a separating funnel and shaken in a mixture of 10% sulphuric acid (30 ml) and ether (70 ml) until all solids had dissolved. The ether layer was removed and washed with 5%

aqueous sodium hydrogen carbonate solution (40 ml) and water (40 ml). Finally, the ether layer was dried (K_2CO_3) and evaporated to dryness to give a liquid product, which on distillation (0.15 mmHg, 165–175 °C) gave the title compound (**6**) (2.60 g, 72%) as a clear liquid (Found: C, 75.45; H, 12.2. Calc. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%); λ_{max}(EtOH) 206 (ε 600 dm^3 mol^{-1} cm^{-1}) and 289 nm (2 250); ν_{max}(liquid film) 3 400 (enolic OH), 2 945, 2 915, and 2 840 (CH), 1 715 and 1 695 (C=O), and 1 600 br (enolic C=O); δ_H(90 MHz, $CDCl_3$) 0.88 (3 H, t, CH_3), 1.26–2.50 [18 H, m, $CH(CH_2)_9$], 2.16 (6 H, CH_3CO), and 3.59 (1 H, t, CH).

Similarly prepared was *3-hexadecylpentane-2,4-dione* (**7**)[13] from nonadecan-2-one (3.00 g, 0.011 mol) in 68% yield as a white solid, m.p. 50–51 °C (Found: C, 77.9; H, 12.65. Calc. for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42%); λ_{max}(EtOH) 210 (ε 550 dm^3 mol^{-1} cm^{-1}) and 283 nm (1 600); ν_{max}(KCl) 2 950, 2 910, and 2 840 (CH), 1 715 and 1 695 (C=O), and 1 600 (enolic C=O); δ_H(90 MHz, $CDCl_3$) 0.88 (3 H, t, CH_3), 1.27–2.50 [30 H, m, $CH(CH_2)_{15}$], 2.17 (6 H, s, $COCH_3$), and 3.60 (1 H, t, CH).

4-Tridecylpyridine (**8**).[14]—A solution of 4-methylpyridine (4.66 g, 0.05 mol) in dry ether (30 ml) was maintained under an atmosphere of nitrogen. To this rapidly stirred solution was added dropwise an ether solution of phenyl-lithium (29 ml, 1.8 N, 0.05 mol) over a period of 1 h. After addition was complete, the resulting mixture was stirred for a further 45 min. 1-Bromododecane (12.46 g, 0.05 mol) in dry ether (40 ml) was then added to the reaction flask over a period of 10 min. Stirring was continued for a further 45 min before water (50 ml) and then concentrated hydrochloric acid (30 ml) were added slowly to the stirred reaction mixture. The reaction flask was then removed from the nitrogen atmosphere and the ether layer, containing a white insoluble solid, was isolated. The white solid was then collected on a Büchner filter funnel and washed with ether (2 × 30 ml) before being transferred into a separating funnel and ether (50 ml) and aqueous sodium hydroxide (5.00 g in 50 ml) were added. On shaking, the white solid disappeared and the aqueous layer was run off. Finally, the ether layer was dried (KOH pellets) and evaporated to dryness to give a liquid product, which on distillation (0.15 mmHg, 220 °C) gave the title compound as a clear liquid (9.29 g, 71%) (Found: C, 82.9; H, 12.35; N, 5.4. Calc. for $C_{18}H_{31}N$: C, 82.69; H, 11.95; N, 5.36%); λ_{max}(cyclohexane) 210 (ε 2 200 dm^3 mol^{-1} cm^{-1}) and 256 nm (1 500); ν_{max}(liquid film) 3 060 and 3 020 (CH, arom.), 2 950, 2 920, and 2 850 (CH, aliph.), and 1 600 cm^{-1} (C–N); δ_H(90 MHz, $CDCl_3$), 0.88 (3 H, t, CH_3), 1.27–1.95 [22 H, m, $(CH_2)_{11}CH_3$], 2.60 (2 H, t, CH_2), 7.06 (2 H, d, arom.), and 8.47 (2 H, d, arom.).

N-(4-Pyridyl)decanamide.[15]—To a stirred solution of 4-aminopyridine (2.00 g, 0.021 mol) and triethylamine (3.75 ml) in dichloromethane (15 ml) was added a solution of decanoyl chloride (4. 45 g, 0.023 mol) in dichloromethane (5 ml) over a 3 h period (throughout this addition the temperature was maintained at 15 °C). This mixture was then warmed on a steam-bath for 2 h before being allowed to cool to room temperature. Dichloromethane (30 ml) was then added and solution transferred to a separating funnel, where it was washed with water (2 × 30 ml). Finally, the organic layer was dried (Na_2CO_3) and evaporated under reduced pressure to give the title compound as a clear liquid (4.07 g, 78%) (Found: C, 71.8; H, 9.8; N, 10.85. Calc. for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28%); ν_{max}(liquid film) 3 240 and 3 150 (NH), 2 950, 2 920, and 2 850 (CH), 1 690 (CO), and 1 600 cm^{-1} (C–N); δ_H(90 MHz, $CDCl_3$) 0.87 (3 H, t, CH_3), 1.26–1.90 [14 H, m, $COCH_2(CH_2)_7$], 2.40 (2 H, t, $COCH_2$), 7.57 (2 H, d, arom.), 8.44 (2 H, d, arom), and 9.26 (1 H, s, NH).

4-(Decylamino)pyridine (**10**).[15]—To a stirred suspension of lithium aluminium hydride (0.96 g, 0.025 mol, 20% excess) in dry tetrahydrofuran (20 ml) under a nitrogen atmosphere was added a solution of *N*-(4-pyridyl)decanamide (5.20 g, 0.021 mol) in dry tetrahydrofuran (20 ml) at a rate sufficient to maintain a gentle reflux (*ca.* 1 h 30 min). The reaction solution was refluxed for a further 7 h on a steam-bath before being cooled to 0 °C, removed from the nitrogen atmosphere, and water (20 ml) added to destroy any excess of lithium aluminium hydride. The solution was then poured into 1M sulphuric acid (300 ml), tetrahydrofuran removed under reduced pressure, and the aqueous solution remaining transferred into a separating funnel and washed with ether (1 × 100 ml). The aqueous layer was then made basic by the addition of sodium hydroxide pellets. This basic solution was extracted with ether (2 × 100 ml) and the combined extracts dried ($MgSO_4$) and evaporated to dryness to give a solid product. This on recrystallisation from benzene gave (**10**) as a white powder (2. 51 g, 51%), m.p. 75 °C (Found: C, 77.25; H, 11.55; N, 11.95. Calc. for $C_{15}H_{26}N_2$: C, 76.87; H, 11.18; N, 11.95%); λ_{max}(EtOH) 207 (ε 16 800 dm^3 mol^{-1} l^{-1}) and 255 nm (11 400); ν_{max}(KCl) 3 220 (NH), 3 010 (CH, arom.), 2 950, 2 910, and 2 840 (CH, aliph.) and 1 600 cm^{-1} (C–N); δ_H(90 MHz, $CDCl_3$) 0.89 (3 H, t, CH_3), 1.30–1.80 [16 H, m, $(CH_2)_8CH_3$], 4.45 (1 H, br s, NH), 6.40 (2 H, d, arom.), and 8.15 (2 H, d, arom.).

[4-(N-Decylamino)pyridinebis(pentane-2,4-dionato)]palladium(II) (**11**).—[Bis(pentane-2,4-dionato)]palladium(II) (0.31 g, 4.3×10^{-4} mol) and 4-(*N*-decylamino)pyridine (0.107 g, 4.56×10^{-4} mol, 6% excess) in dichloromethane (1 ml) were stirred for 30 min. Light petroleum (b.p. 60–80 °C; 5 ml) was then added and this solution, on partial removal of solvent under reduced pressure, gave orange crystals of (**11**), which were filtered off (0.211 g, 91%) (Found: C, 53.95; H, 7.55; N, 5.1. Calc. for $C_{25}H_{40}N_2O_4Pd$: C, 55.71; H, 7.48; N, 5.20%); ν_{max}(KCl) 3 300 (NH), 2 950, 2 920, and 2 850 (CH), 1 670 (C=O), and 1 580 cm^{-1} (C–N/C–O); δ_H(90 MHz, $CDCl_3$) 0.89 [3 H, t, $(CH_2)_8CH_3$], 1.29–1.90 [16 H, m, $(CH_2)_8CH_3$], 1.92 and 2.00 (6 H, two singlets, $COCH_3$ *cis* and *trans* respectively to aminopyridine ligand of pentane-2,4-dionate ligand that is oxygen-chelated to palladium), 2.21 (6 H, s, $COCH_3$ of pentane-2,4-dionato ligand that is carbon-bonded to palladium), 3.11 (2 H, q, $NHCH_2$), 4.28 (1 H, s, methine proton of C–Pd bonded pentane-2,4-dionate ligand), 5.36 (1 H, s, methine proton of O–Pd bonded pentane-2,4-dionate ligand), 5.80 (1 H, s, NH), 6.46 (2 H, d, arom.), and 8.00 (2 H, d, arom.).

N-Butylsalicylideneamine (**12b**).—Butylamine (36.5 g, 0.5 mol) was added to a solution of salicylaldehyde (30.5 g, 0.25 mol) in refluxing dry acetonitrile (120 ml) over a period of 15 min. The mixture was then heated under reflux for a further 30 min after which it was allowed to cool to room temperature when solvent and excess of amine were removed under reduced pressure. Distillation (0.2 mmHg; 87 °C) gave (**12b**) as a yellow liquid (41.52 g, 93.8%) (Found: C, 74.15; H, 8.55; N, 8.2. Calc. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90%); ν_{max}(liquid film) 3 050 (CH, arom.), 2 950, 2 920, and 2 850 (CH, aliph.), 2 800 (br OH) and 1 630 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 0.95 (3 H, t, CH_3), 1.55 (4 H, m, $CH_2CH_2CH_3$), 3.55 (2 H, t, NCH_2), 6.70–7.45 (4 H, m, arom.), 8.31 (1 H, s, CH=N), and 13.4 (1 H, s, OH). The following were similarly prepared.

N-Dodecylsalicylideneamine (**12c**) (92%), m.p. 37 °C (from ethanol–benzene) (Found: C, 78.75; H, 10.7; N, 4.75. Calc. for $C_{19}H_{31}NO$: C, 78.84; H, 10.80; N, 4.84%); ν_{max}(KCl) 3 050 (CH, arom.), 2 950, 2 910, and 2 840 (CH, aliph.), 2 700 (br OH), and 1 630 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 0.89 (3 H, t, CH_3), 1.28–2.00 [20 H, m, $(CH_2)_{10}CH_3$], 3.56 (2 H, t, NCH_2),

6.70–7.40 (4 H, m, arom.), 8.30 (1 H, s, CH=N), and 13.51 (1 H, br s, OH).

N-*Octadecylsalicylideneamine* (**12d**) (92%), m.p. 40–41 °C (from ethanol–benzene) (Found: C, 80.15; H, 11.5; N, 3.8. Calc. for $C_{25}H_{43}NO$: C, 80.34; H, 11.51; N, 3.75%; ν_{max}(KCl) 3 050 (CH, arom.), 2 950, 2 910, and 2 850 (CH, aliph.), 2 800 (br OH), and 1 630 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 0.88 (3 H, t, CH_3), 1.28–2.00 [32 H, m, $(CH_2)_{16}CH_3$], 3.57 (2 H, t, NCH_2), 6.70–7.40 (4 H, m, arom.), 8.30 (1 H, s, CH=N), and 13.53 (1 H, br s, OH).

Bis(N-*methylsalicylideneaminato*)*palladium*(II) (**13a**).—Palladium dichloride (0.580 g, 3.27×10^{-3} mol), 2-*N*-methylsalicylideneamine (0.911 g, 6.74×10^{-3} mol, 3% excess), and triethylamine (0.682 g, 6.74×10^{-3} mol, 3% excess) were stirred in absolute methanol (40 ml) at 50–60 °C for 24 h. The crude light green–yellow solid product was then filtered off and recrystallised from an ethanol–benzene mixture to give yellow crystals of (**13a**) (0.96 g, 78%), m.p. 276–277 °C (Found: C, 50.9; H, 4.25; N, 7.35. Calc. for $C_{16}H_{16}N_2O_2Pd$: C, 51.29; H, 4.30; N, 7.48%); ν_{max}(KCl) 3 040 and 3 020 (CH, arom.), 2 930 and 2 910 (CH, aliph.), and 1 625 cm^{-1} (C=N); $\lambda_{max}(CH_2Cl_2)$ 241 (ε 56 900 dm^3 mol^{-1} l^{-1}) and 390 nm (5 900); δ_H(250 MHz, [$^2H_6$]-DMSO) 3.424 (6 H, s, CH_3), 6.557 (2 H, t, arom.), 6.811 (2 H, d, arom.), 7.263 (2 H, t, arom.), 7.351 (2 H, d, arom.), and 8.058 (2 H, s. CH=N).

Bis(N-*butylsalicylideneaminato*)*palladium*(II) (**13b**).—*Method* 1. Palladium dichloride (0.100 g, 5.64×10^{-4} mol) was dissolved in the minimum amount of hot aqueous 1M potassium chloride (60 ml). Sodium acetate trihydrate (0.215 g, 1.18×10^{-3} mol, 5% excess) was then dissolved in this solution before it was added to a solution of *N*-butylsalicylideneamine (0.21 g, 1.18×10^{-3}, 5% excess) dissolved in acetone (40 ml). The resulting mixture was refluxed on a steam-bath for 30 min and then left to cool to room temperature. Solvent acetone was then removed under reduced pressure and the resulting solid was filtered off and washed with methanol. Recrystallisation of this solid from ethanol–benzene gave yellow crystals of (**13b**) (0.21 g, 80%), m.p. 187–188 °C (Found: C, 57.2; H, 6.15; N, 6.0. Calc. for $C_{22}H_{28}N_2O_2Pd$: C, 57.88; H, 6.15; N, 6.10%); ν_{max}(KCl) 3 020 (CH, arom.), 2 950 and 2 920 (CH, aliph.), and 1 615 cm^{-1} (C=N); $\lambda_{max}(CH_2Cl_2)$ 241 (ε 57 300 dm^3 mol^{-1} l^{-1}) and 394 nm (6 100); δ_H(90 MHz, $CDCl_3$), 0.96 (6 H, t, CH_3), 1.42 (4 H, m, CH_2CH_3), 1.78 (4 H, quintet, NCH_2CH_2), 3.71 (4 H, t, NCH_2), 6.55–7.23 (8 H, m, arom.), and 7.58 (2 H, s, CH=N).

Method 2. Palladium dichloride (0.580 g, 3.27×10^{-3} mol), *N*-butylsalicylideneamine (1.194 g, 6.74×10^{-3} mol, 3% excess) and triethylamine (0.682 g, 6.74×10^{-3} mol, 3% excess) were stirred together in absolute methanol (40 ml) at 50–60 °C for 24 h. The crude light green–yellow solid product was then filtered off and recrystallised from an ethanol–benzene mixture to give yellow crystals of (**13b**) (1.10 g, 73%). Characterisation was as for (**13b**) above. Similarly prepared were the following.

Bis(N-*dodecylsolicylideneaminato*)*palladium*(II) (**13c**). This compound was prepared by Method 1 (75%) and Method 2 (70%). Recrystallisation of the products from an ethanol–benzene afforded yellow needles of (**13c**) (0.29 g, 75%), m.p. 115–116 °C (Found: C, 66.5; H, 8.7; N, 4.0. Calc. for $C_{38}H_{60}N_2O_2Pd$: C, 66.74; H, 8.85; N, 4.10%); ν_{max}(KCl) 3 040 and 3 020 (CH, arom.), 2 910 and 2 840 (CH, aliph.), and 1 615 cm^{-1} (C=N); $\lambda_{max}(CH_2Cl_2)$ 241 (ε 62 900 dm^3 mol^{-1} l^{-1}) and 394 nm (6 670); δ_H(90 MHz, $CDCl_3$) 0.88 (6 H, t, CH_3), 1.26–2.00 [40 H, m, $NCH_2(CH_2(CH_2)_{10}]$, 3.69 (4 H, t, NCH_2), 6.54–7.22 (8 H, m, arom.), and 7.57 (2 H, s, CH=N).

Bis(N-*octadecylsalicylideneaminato*)*palladium*(II) (**13d**). This compound was prepared by Method 1 (77%) and Method 2 (67%). Recrystallisation of the product from ethanol–benzene afforded yellow needles of (**13d**), m.p. 104–105 °C (Found: C, 70.35; H, 9.9; N, 3.25. Calc. for $C_{50}H_{84}N_2O_2Pd$: C, 70.52; H, 9.94; N, 3.29%); ν_{max}(KCl) 3 040 and 3 020 (CH, arom.), 2 910 and 2 840 (CH, aliph.), and 1 615 cm^{-1} (C=N); $\lambda_{max}(CH_2Cl_2)$ 241 (ε 61 800 dm^3 mol^{-1} l^{-1}) and 394 nm (6 800); δ_H(90 MHz, $CDCl_3$) 0.88 (6 H, t, CH_3), 1.26–2.00 [64 H, m, $NCH_2(CH_2)_{32}$], 3.70 (4 H, t, NCH_2), 6.55–7.24 (8 H, m, arom.), and 7.58 (2 H, s, CH=N).

Bis(N-*phenylsalicylideneaminato*)*palladium*(II) (**13e**). This compound was prepared by Method 2. Recrystallisation from ethanol–benzene gave yellow crystals of (**13e**) (1.34 g, 82%), m.p. >305 °C (decomp) (Found: C, 62.4; H, 3.9; N, 5.45. Calc. for $C_{26}H_{20}N_2O_2Pd$: C, 62.60; H, 4.04; N, 5.62%); ν_{max}(KCl) 3 050 and 3 010 (CH, arom.) and 1 600 cm^{-1} (C=N); δ_H(250 MHz, [$^2H_6$]-DMSO) 5.907 (2 H, d, arom.), 6.483 (2 H, t, arom.), 7.121 (2 H, t, arom.), 7.121 (2 H, t, arom.), 7.306–7.456 (12 H, m, arom.), and 8.072 (2 H, s, CH=N); $\lambda_{max}(CH_2Cl_2)$ 249 (ε 60 200 dm^3 mol^{-1} l^{-1}), 291 (19 500), and 413 nm (7 100).

[N,N′-*Ethylenebis*(*salicylideneaminato*)]*palladium*(II) [*Forms* (**14**) *and* (**15**)]. Method 1 gives the yellow isomer of Pd-salen (**14**) only.

Recrystallisation from DMF gave yellow needles of (**14**) which were high vacuum dried (0.52 g, 62%), m.p. >320 °C (decomp.) (Found: C, 51.8; H, 3.8; N, 7.6. Calc. for $C_{16}H_{14}N_2O_2Pd$: C, 51.56; H, 3.79; N, 7.52%); ν_{max}(KCl) 3 060, 3 030, and 3 010 (CH, arom.), 2 920 (CH, aliph.), and 1 625 cm^{-1} (C=N); $\lambda_{max}(CH_2Cl_2)$ 241 (ε 43 600 dm^3 mol^{-1} l^{-1}), 399 (6 300), and 412 nm (6 280); δ_H(250 MHz, [^2H]$_6$-DMSO) 3.820 (4 H, s, CH_2CH_2), 6.542 (2 H, t, arom.), 6.705 (2 H, d, arom.), 7.246–7.387 (4 H, m, arom.), and 8.192 (2 H, s, CH=N).

Method 2, Baryshnikov's method,[8] gives the yellow (**14**) and green (**15**) isomers of Pd-salen. Palladium dichloride (0.75 g, 4.23×10^{-3} mol), salen (1.17 g, 4.36×10^{-3}, 3% excess), and triethylamine (0.88 g, 8.70 mmol, 3% excess) were stirred together in absolute methanol (50 ml) at 50–60 °C for 6 h, or until 1 h after a very noticeable colour change, from light green to dark green, took place in the contents of the reaction flask (whichever was longer). The reaction was then stopped and the crude green solid product was collected by suction filtration and washed with methanol (weight: 1.60 g, 100%).

The crude product was then separated into the yellow (**14**) and green (**15**) isomers of Pd-salen. This was achieved by shaking up the crude reaction product in steam-bath heated DMF (200 ml; maximum temperature 60 °C) and suction filtering the solution. The dark green solid that collected on the filter paper was then shaken up in warm DMF (2 × 200 ml; maximum temperature 60 °C) and collected by suction filtration at least two more times (that is, until the DMF filtrate became clear). Finally, the DMF filtrate was concentrated under reduced pressure until a yellow solid precipitated out of solution and this was collected and recrystallised from DMF to give yellow needles of (**14**) (0.69 g, 44%); characterisation as (**14**) prepared *via* Method 1. The insoluble green solid that collected on the filter paper was shaken up in warm chloroform (150 ml), collected by suction filtration, and dried *in vacuo* to give the green insoluble isomer of Pd-salen (**15**) as a powder (0.44 g, 28%), m.p. >200 °C (decomp.) (Found: C, 52.15; H, 3.85; N, 7.65. Calc. for $C_{16}H_{14}N_2O_2Pd$: C, 51.56; H, 3.79; N, 7.52%); ν_{max}(KCl) 3 040 and 3 010 (CH, arom), 2 940 and 2 920 (CH, aliph.), and 1 615 cm^{-1} (C=N). M^+, 372 (for Pd^{106}).

5-*Propylsalicylaldehyde* (**17a**).[16]—A mixture of sodium hydroxide (11.9 g, 0.3 mol) suspended in water (12 ml) and a solution of *p*-propylphenol (9.00 g, 0.066 mol) in methanol (25 ml) was stirred and maintained at 60 °C as chloroform (33 ml, 0.41 mol) was added dropwise. On completion of this addition, the resulting mixture was stirred and kept at 60 °C

for a further 2 h, before being allowed to cool and subsequently acidified (to pH 5) using 10% hydrochloric acid. Water (30 ml) was then added and the solution transferred to a separating funnel and the aqueous layer run off. The organic layer was then washed with water (2 × 50 ml) before solvent was removed under reduced pressure to give a crude organic product. This was purified by adding to it about twice its volume of a saturated aqueous sodium metabisulphite and subjecting this mixture to vigorous mechanical shaking for 45 min; it was then set aside for 1 h. After this the bisulphite paste was suction filtered and washed with ether and ethanol to remove all unchanged starting material. The pure bisulphite adduct was then decomposed by warming it with dilute sulphuric acid. On cooling, this solution was extracted with ether (2 × 100 ml) and the combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give (**17a**) as a clear liquid (1.95 g, 18%) (Found: C, 71.95; H, 7.3. Calc. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%); ν_{max}(liquid film) 3 180br (OH), 3 060 and 3 020 (CH, arom.), 2 960, 2 930, and 2 870 (CH, aliph.), 2 740 (CH, aldehyde), and 1 660 cm^{-1} (C=O); δ_H(90 MHz, $CDCl_3$) 0.95 (3 H, t, CH_3), 1.64 (2 H, m, $ArCH_2CH_2$), 2.58 (2 H, t, $ArCH_2$), 6.83–7.40 (3 H, m, arom.), 9.85 (1 H, s, CHO), and 10.83 (1 H, s, OH).

Similarly prepared was *5-t-butylsalicylaldehyde* (**17b**)[16] from 4-t-butylphenol in 19% yield (Found: C, 73.25; H, 7.8. Calc. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%); ν_{max}(liquid film) 3 200 br (OH), 3 060 and 3 020 (CH, arom.), 2 960 (CH, aliph.), 2 730 (CH, aldehyde), and 1 655 cm^{-1} (C=O); δ_H(90 MHz, $CDCl_3$) 1.32 (9 H, s, Bu^t, 6.80–7.64 (3 H, m, arom.), 9.85 (1 H, s, CHO), and 10.83 (1 H, s, OH).

N,N′-*Ethylenebis*(*5-propylsalicylideneamine*) (**18a**).—5-Propylsalicylideneamine (**17a**) (2.00 g, 0.012 mol) and ethane-1,2-diamine (0.36 g, 6 × 10^{-3} mol) in dry acetonitrile (25 ml) were refluxed for 30 min. The solvent was then removed under reduced pressure and the solid obtained recrystallised from ethanol to give yellow crystals of (**18a**) (1.61 g, 71%), m.p. 129 °C (Found: C, 73.9; H, 7.4; N, 8.05. Calc. for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95%); ν_{max}(KCl) 2 950, 2 920, and 2 860 (CH, aliph.), 2 750br (intramolecular OH), and 1 630 cm^{-1} (C=N); δ_{max}(90 MHz, $CDCl_3$), 0.92 (6 H, t, CH_3), 1.59 (4 H, m, $ArCH_2CH_2$), 2.51 (4 H, t, $ArCH_2$), 3.90 (4 H, s, NCH_2CH_2N), 6.80–7.23 (6 H, m, arom.), 8.30 (2 H, s, CH=N), and 12.89 (2 H, br s, OH). Similarly prepared were the following compounds.

N,N′-*Ethylenebis*(*5-t-butylsalicylideneamine*) (**18b**) (76%), m.p. 170–171 °C (from ethanol) (Found: C, 75.9; H, 8.55; N, 7.25. Calc. for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36%); ν_{max}(KCl) 2 950, 2 900, and 2 860 (CH, aliph.), 2 700br (intramolecular OH), and 1 630 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 1.27 (18 H, s, Bu^t), 3.89 (4 H, s, NCH_2CH_2N), 6.80–7.47 (6 H, m, arom.), 8.32 (2 H, s, CH=N), and 12.86 (2 H, br s, OH).

N,N′-*Ethylenebis*(*5-chlorosalicylideneamine*) (**18c**) (58%), m.p. 180 °C (from acetone) (Found: C, 57.2; H, 4.1; Cl, 20.9; N, 8.25. Calc. for $C_{16}H_{14}Cl_2N_2O_2$: C, 56.99; H, 4.18; Cl, 21.03; N, 8.31%); ν_{max}(KCl) 2 890 and 2 840 (CH, aliph.) 2 750br (OH) and 1 625 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 3.92 (NCH_2CH_2N), 6.73–7.31 (6 H, m, arom.), 8.26 (2 H, s, CH=N), and 12.98 (2 H, s, OH).

N,N′-(*Ethylenebis*(*5-methylsalicylideneamine*) (**18d**) (61%), m.p. 170 °C (from acetonitrile) (Found: C, 72.8; H, 6.7; N, 9.5. Calc. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45%); ν_{max}(KCl) 2 950, 2 910, and 2 850 (CH, aliph.), 2 740br (OH) and 1 625 cm^{-1} (C=N); δ_H(90 MHz, $CDCl_3$) 2.26 (6 H, s, CH_3), 3.90 (4 H, s, NCH_2CH_2N), 6.75–7.20 (6 H, m, arom.), 8.26 (2 H, s, CH=N), and 12.77 (2 H, br s, OH).

[N,N′-*Ethylenebis*(*5-propylsalicylideneaminato*)]*palladium*-(II) (**19a**).—This compound was prepared by Method 2. Recrystallisation from chloroform gave (**19a**) as a yellow microcrystalline solid (0.53 g, 69%), m.p. >320 °C (decomp.) (Found: C, 56.85; H, 5.65; N, 5.95. Calc. for $C_{22}H_{26}N_2O_2Pd$: C, 57.84; H, 5.74; N, 6.13%); ν_{max}(KCl) 2 950, 2 920, and 2 850 (CH, aliph.) and 1 625 cm^{-1} (C=N); λ_{max}(CH_2Cl_2) 242 (ε 44 700 dm^3 mol^{-1} l^{-1}) and 425 nm (6 750); δ_H(250 MHz, $CDCl_3$), 1.551 (4 H, m, $ArCH_2CH_2$), 2.381 (4 H, t, $ArCH_2$), 3.768 (4 H, s, NCH_2CH_2N), 6.543–7.101 (6 H, m, arom.), and 7.157 (2 H, s, CH=N).

During the recrystallisation of (**19a**) a quantity of a black insoluble solid collected on the filter paper. This was shaken up in hot chloroform, collected by suction filtration, and allowed to dry to give a black insoluble solid (0.023 g, 3%) (Found: C, 40.4; H, 3.9; Cl, 2.55; N, 4.15%); ν_{max}(KCl) 2 920 (CH, aliph.) and 1 620br cm^{-1} (C=N); M^+, 456 (for Pd^{106}). Similarly prepared were the following compounds.

[N,N′-*Ethylenebis*(*5-t-butylsalicylideneaminato*)]*palladium*(II) (**19b**). Recrystallisation from chloroform gave (**19b**) as a yellow microcrystalline solid (0.56 g, 68%), m.p. >300 °C (decomp.) (Found: C. 58.7; H, 5.95; N, 5.6. Calc. for $C_{24}H_{30}N_2O_2Pd$: C, 59.45; H, 6.24; N, 5.78%); ν_{max}(KCl) 2 950, 2 890, and 2 850 (CH, aliph.) and 1 625 cm^{-1} (C=N); λ_{max}(CH_2Cl_2) 239 (ε 47 300 dm^3 mol^{-1} l^{-1}) and 423 nm (6 450); δ_H(250 MHz, $CDCl_3$) 1.265 (18 H, s, Bu^t), 3.782 (4 H, s, NCH_2CH_2N), 7.090–7.419 (6 H, m, arom.), and 7.740 (2 H, s, CH=N).

During the recrystallisation of (**19b**) a quantity of a black insoluble solid collected on the filter paper. This was shaken up in hot chloroform, collected by suction filtration, and allowed to dry to give a black insoluble solid (0.033 g, 4%) (Found: C, 42.0; H, 4.7; Cl, 2.70; N, 4.15%); ν_{max}(KCl) 2 940 (CH, aliph.) and 1 615br cm^{-1} (C=N); M^+, 484 (for Pd^{106}).

[N,N′-*Ethylenebis*(*5-chlorosalicylideneaminato*)]*palladium*-(II) (**19c**).—The yellow solid product was recrystallised from DMF to give crystals of (**19c**) (1.07 g, 74%), m.p. >325 °C (decomp.) (Found: C, 43.35; H, 2.8; Cl, 16.05; N, 6.4. Calc. for $C_{16}H_{12}Cl_2N_2O_2Pd$: C, 43.52; H, 2.74; Cl, 16.06; N, 6.34%); ν_{max}(KCl) 3 040 (CH, arom.), 2 920 (CH, aliph.) and 1 625 cm^{-1} (C=N); δ_H(250 MHz, [$^2H_6$]-DMSO) 3.841 (4 H, s, NCH_2CH_2N), 7.843 (2 H, d, arom.), 7.288 (2 H, d, arom.), 7.445 (2 H, s, arom.), and 8.183 (2 H, s, CH=N); λ_{max}(CH_2Cl_2) 247 (ε 44 100 dm^3 mol^{-1} l^{-1}), 410 (5 250), and 428 nm (5 650).

[N,N′-*Ethylenebis*(*5-methylsalicylideneaminato*)]*palladium*-(II) (**19d**). The yellow solid remaining was recrystallised from DMF to give crystals of (**19d**) (0.90 g, 69%), m.p. >310 °C (decomp.) (Found: C, 53.5; H, 4.55; N, 7.05. Calc. for $C_{18}H_{18}N_2O_2Pd$: C, 53.95; H, 4.53; N, 6.99%); ν_{max}(KCl) 3 080 and 3 050 (CH, arom.), 2 980, 2 900, and 2 850 (CH, aliph.), and 1 625 cm^{-1} (C=N); δ_H(250 MHz, [$^2H_6$]-DMSO) 2.171 (6 H, s, CH_3), 3.807 (4 H, s, NCH_2CH_2N), 6.739 (2 H, d, arom.), 7.122 (4 H, m, arom.), and 8.118 (2 H, s, CH=N); λ_{max}(CH_2Cl_2) 240 (ε 43 700 dm^3 mol^{-1} l^{-1}) and 426 nm (6 600).

[N,N′-*Trimethylenebis*(*salicylideneaminato*)]*palladium*(II) (**20**) (70%) m.p. >300 °C (decomp.) (from DMF) (Found: C, 51.95; H, 4.05; N, 7.2. Calc. for $C_{17}H_{16}N_2O_2Pd$: C, 52.80; H, 4.17; N, 7.24%); ν_{max}(KCl) 3 050 and 3 020 (CH, arom.), 2 920 and 2 850 (CH, aliph.), and 1 615 cm^{-1} (C=N); λ_{max}(CH_2Cl_2) 243 (ε 50 200 dm^3 mol^{-1} l^{-1}), 313 (5 800), and 394 nm (6 200); δ_H(250 MHz, [$^2H_6$]-DMSO) 1.969 (2 H, quintet, $NCH_2CH_2CH_2N$), 3.736 (4 H, t, $NCH_2CH_2CH_2N$), 6.518 (2 H, t, arom.), 6.736 (2 H, d, arom.), 7.280 (4 H, m, arom.), and 7.981 (2 H, s, CH=N); M^+, ion 386 (for Pd^{106}).

An insoluble dark green solid was collected during purification of (**20**). The green solid shaken in warm chloroform (150 mol), collected by suction filtration and high vacuum dried to give the green insoluble solid (**33b**) (0.22 g, 10%), m.p. >150 °C (decomp.) (Found: C, 42.65; H, 3.15; Cl, 1.28; N, 5.95.

Calc. for $C_{17}H_{16}N_2O_2Pd$: C, 52.80; H, 4.17; N, 7.24%); ν_{max}(KCl) 1 615 cm^{-1} (C=N); M^+, 386 (for Pd^{106}).

[N,N′-(1-*methylethylenebis*(*salicylideneaminato*)]*palladium*-(II) (**21**) (80%) m.p. >310 °C (from DMF) (decomp.) (Found: C, 52.35; H, 4.0; N, 7.15. Calc. for $C_{17}H_{16}N_2O_2Pd$: C, 52.80; H, 4.17; N, 7.24%); ν_{max}(KCl) 3 070, 3 040, and 3 010 (CH, arom.), 2 960 and 2 920 (CH, aliph.), and 1 625 cm^{-1} (C=N); δ_H(250 MHz, [$^2H_6$]-DMSO) 1.339 (3 H, d, CH_3), 3.950 [1 H, m, NC*H*(CH_3)], 4.001 (2 H, m, CH_2), 6.553 (2 H, t, arom.), 6.831 (2 H, d, arom.), 7.340 (4 H, m, arom.), and 8.201 and 8.178 (2 H, two singlets, CH=N); λ_{max}(CH_2Cl_2) 240 (ε 38 900 dm^3 mol^{-1} l^{-1}, 400 (5 450), and 414 nm (5 650).

[N,N′-o-*phenylenebis*(*salicylideneaminato*)]*palladium*(II) (**22**) (78%), m.p. >320 °C (from DMF–water) (decomp.) (Found: C, 56.65; H, 3.35; N, 6.5. Calc. for $C_{20}H_{14}N_2O_2Pd$: C, 57.09; H, 3.35; N, 6.66%); ν_{max}(KCl) 3 080 and 3 040 (CH, arom.) and 1 600 cm^{-1} (C=N); δ_H(250 MHz, [$^2H_6$]-DMSO) 6.706 (2 H, t, arom.), 7.009 (2 H, d, arom.), 7.435 (4 H, m, arom.), 7.730 (2 H, d, arom.), 8.335 (2 H, m, arom.), and 9.186 (2 H, s, CH=N); λ_{max}(CH_2Cl_2) 251 (ε 38 100 dm^3 mol^{-1} l^{-1}), 316 (23 800), 340 (22 500), 357 (24 900), 381 (10 400), and 480 nm (13 900).

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