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Preparation and reactions of rhodium complexes of some alkenyloxy- and alkenylamino-benzylamines and related compounds: a comparison with catalytic reactions

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Abstract

Reactions of several allyloxy- and allylamino-benzylamines and a benzamide with $[Rh(CO)_2Cl]_2$ give monodentate rhodium complexes which show no evidence of alkene coordination. Reaction of these and related compounds with $HRh(CO)(PPh_3)_3$ give products arising from double bond isomerisation followed by cyclisation or liberation of propene. The results are compared with rhodium-catalysed reactions of these substrates with H_2/CO. © 1997 Published by Elsevier Science S.A.

Keywords: Rhodium; Stoichiometric complexes; Catalysis; Rearrangement; Cyclisation; Allylic cleavage

1. Introduction

We have previously described the preparation of quinazoline and oxazine derivatives by the rhodium-catalysed reaction of functionalised alkenes with carbon monoxide and hydrogen [1–4]. During the investigation some remarkable examples of regioselectivity were exhibited by the allylic substrates. It was of interest to prepare some rhodium complexes of these substrates in an attempt to model the role of the rhodium species in the catalytic reaction cycle. Therefore, it was decided to prepare dicarbonylrhodium(I) complexes of these substrates and to analyse the coordinating properties of the chelate donors by spectroscopic methods. The preparative procedure employed was based on that of Krafft and coworkers who have published extensively in this area [5,6]. We have recently described the preparation of rhodium complexes of some alkynylamines using this method [7].

In another series of reactions, the allylic substrates were reacted with carbonyltris(triphenylphosphine)-rhodium(I) hydride, $HRh(CO)(PPh_3)_3$, and the reaction monitored by ^1H NMR spectroscopy. It was anticipated that $HRh(CO)(PPh_3)_3$ would behave in similar fashion to the active catalyst in the catalytic cycle, as it has both a hydride and a carbonyl group capable of being transferred to the substrate. The reactions were hoped to lead to the identification of possible intermediates present in the catalytic cycle.

2. Results and discussion

2.1. Reactions involving $[Rh(CO)_2Cl]_2$

The allylic substrates **1** to **4** were reacted with $[Rh(CO)_2Cl]_2$ in hexane at ambient temperature. The resulting complexes **5–8** were recovered by filtration and, where necessary, purified by chromatography and crystallisation.

The diamines **1** and **2** gave complexes **5** and **6** respectively, both of which showed evidence for the rhodium atom coordinating to both nitrogen atoms in that both of the aminomethylene protons in each complex showed a significant downfield shift in the ^1H NMR spectrum. Similar shifts were reported by Krafft and Wilson [5]. There was no evidence to suggest that coordination of the olefin to the metal centre had oc-

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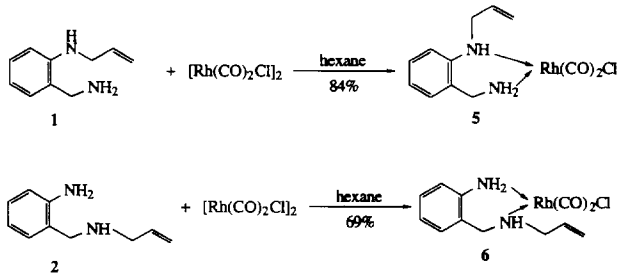
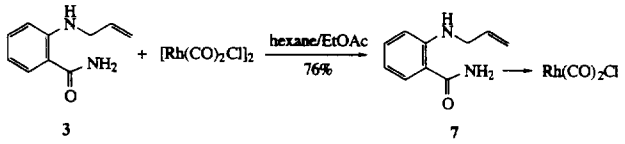
curred as there was no significant change in the chemical shifts of the alkene protons in the ^{1}H NMR spectra.



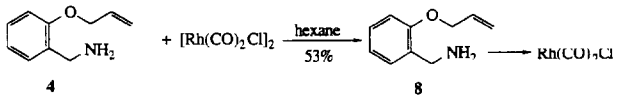
A reaction of an allylic amine by Krafft resulted in the formation of a monodentate ligand complex and attempts to force the addition of the olefin were unsuccessful. Krafft and Wilson suggest that the preference of the C=C bond to be orthogonal to the coordination square plane in Rh(I) complexes results in allylic amines having a chelation ring size which is too small to allow proper orbital overlap necessary to achieve the desired orthogonal coordination [5]. However, the compound **1** also possesses a benzylamine function and it has been proposed that additional coordination of this amine to a rhodium atom may be responsible for the regiospecificity of the rhodium-catalysed reaction of **1** with H_2/CO [1]. A related argument involving the anilino nitrogen in **2** could be used to account for the analogous regiospecificity seen in the catalytic reaction of **2** with H_2/CO [2].

The related amide **3** was reacted with $[Rh(CO)_2Cl]_2$ in hexane–ethyl acetate. The ^{1}H and ^{13}C NMR spectra of resulting complex **7** showed no significant shifts in any of the protons or carbon atoms suggesting that coordination was restricted to the amide function. The infrared spectrum of **7** showed an increase in the carbonyl stretching frequency (of ca. 20 cm^{-1}) suggesting that coordination to rhodium is through the nitrogen atom [8].



Again, rhodium-catalysed reaction of **3** with H_2/CO was regiospecific leading to formation of a [1,2-*a*]-pyrroloquinazolinone. It is possible that the aniline nitrogen does coordinate with the rhodium under hydroformylation conditions as was observed for compound **2**.

Reaction of the allyloxy compound **4** under the same conditions gave **8** as a blood red solid.



The ^{1}H NMR spectrum again showed a downfield shift of the aminomethylene protons and no shifts in either the ether methylene or olefinic protons, suggesting coordination was only to nitrogen. Catalytic reaction of **4** with H_2/CO gives a product arising from cleavage and regiospecific carbonylation of the allyl group [3,4]. A solution of complex **8** in ethyl acetate was heated in an attempt to induce bidentate coordination involving the alkenyl as well as the amino function as described by Krafft and Wilson [5]. Only a small amount of decomposition was observed. The complex was unreactive towards carbon monoxide (400 lbf in^{-2}, 80 °C, 5 h) but reacted with hydrogen (120 lbf in^{-2}, 60 °C, 6 h) to give mainly the propyloxy analogue of **8** arising from hydrogenation of the double bond together with the phenolic complex arising from allylic cleavage.

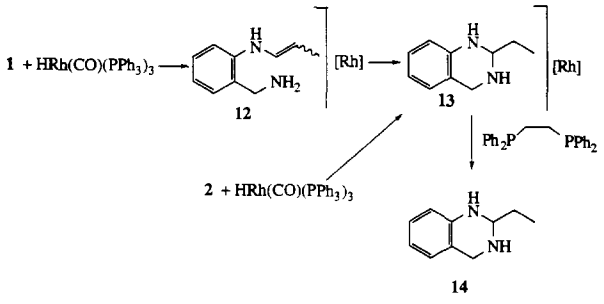
The infra-red spectrum of the substituted benzylamine complex **8** shows two intense bands in the carbonyl region (2000–2100 cm^{-1}) and is very similar to the spectrum of the parent benzylamine complex $PhCH_2NH_2Rh(CO)_2Cl$ [9]. This latter complex has been shown to be monomeric, square-planar and non-ionic based on NMR, UV, IR and conductance data [9]. The complexes **5**, **6**, and **7** have similar spectra, which suggests a similar square-planar structure with possibly the additional nitrogen in compounds **5** and **6** occupying an apical position (giving a square pyramidal complex).

The compounds showed a similar colour variation between solid (yellow/orange/red) and solution (pale yellow) as described previously [9] and attributed to crystal stacking leading to interactions through Rh(1) centres.

2.2. *Reactions involving $HRhCO(PPh_3)_3$*

Reactions of the allylic substrates **1**, **2**, **4** and **9**, **10** and the butenyl homologue **11** were carried out in sealed NMR tubes in degassed d_6-benzene at 40 or 60 °C. The reactions were monitored by ^{1}H NMR spectroscopy. The resulting rhodium complexes were not isolated but characterised by ^{1}H NMR and where appropriate the newly formed heterocyclic ligands were isolated after decomplexation and characterised by spectro-

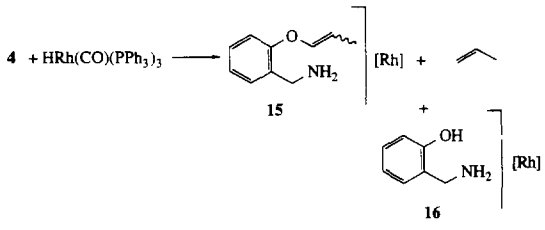
scopic means including comparison with authentic samples.



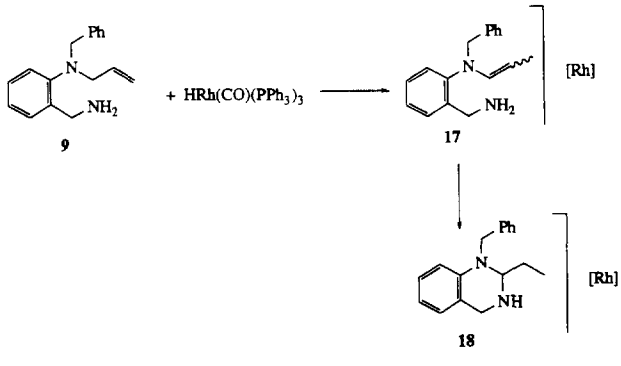
Reactions of the allylamines **1** and **2** first involved isomerisation of the double bond to form *cis*- and *trans*-enamines, e.g. **12** which cyclised to form the same 2-ethylquinazoline complex **13** from which a sample of the free quinazoline **14** was obtained. It was not possible to isolate the complex **13**, e.g. attempted chromatography on silica led to decomplexation and isolation of **14**. The nucleophilic attack of an amino group on a coordinated double bond is well documented and has been used for the preparation of heterocyclic compounds (see Ref. [10]; for a review see Ref. [11]). A perhaps more closely related example which must involve double bond isomerisation as well as cyclisation is the rhodium-catalysed formation of an anilinoquinoline from *N*-allylaniline [12]. Further isomerisation could give imines (or in a later case, e.g. from **9**, an imonium salt) but no evidence for their formation was obtained from the ^{1}H NMR spectra.

The rapid isomerisation of **1** and **2** at 60 °C in the presence of $HRh(CO)(PPh_3)_3$ is in contrast with the rhodium-catalysed reactions of these substrates with H_2/CO at 80 °C which give products in near quantitative yield arising from an initial regiospecific terminal hydroformylation [1,2]. No evidence for products arising from alkene isomerisation was obtained.

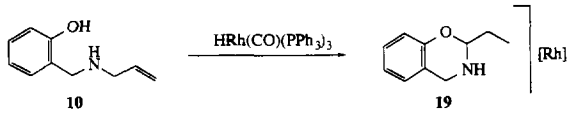
Reaction of the allyloxy compound **4** under these conditions showed an initial rapid isomerisation of the double bond to form a mixture of the *cis*- and *trans*-internal alkenes together with some propene. The starting material had mainly been consumed in ca. 10 min. After 30 min, the spectra showed an approximate equimolar mixture of propene and the alkene complexes **15** (ca. 3:1, *cis*:*trans*) and the ratio of products did not change on further standing. The uncoordinated propene was readily removed by blowing a stream of nitrogen through the reaction mixture. It is interesting that the benzylamine did not attack the isomerised alkene in complex **15**, nor any coordinated propene, and that no π-allyl rhodium compounds were observed. The reaction parallels the rhodium-catalysed reaction of this substrate with H_2/CO only in that cleavage of the allyl group occurs in both reactions [3,4].



Rhodium-catalysed reaction of the *N*-benzyl analogue of **1**, i.e. **9**, with H_2/CO has been shown to give a product arising from a similar reaction sequence to that of the allyloxybenzylamine **4** [3,4]. Stoichiometric reaction with $HRhCO(PPh_3)_3$ did not parallel either the catalytic reactions of itself or **4** nor the stoichiometric reaction of **4** in that no allyl cleavage was observed. The reaction sequence was identical to that described for the *N*-allyl compound **1** involving rapid isomerisation to a mixture of *cis*- and *trans*-alkenes **17** followed by cyclisation to the 2-ethylquinazoline **18**.

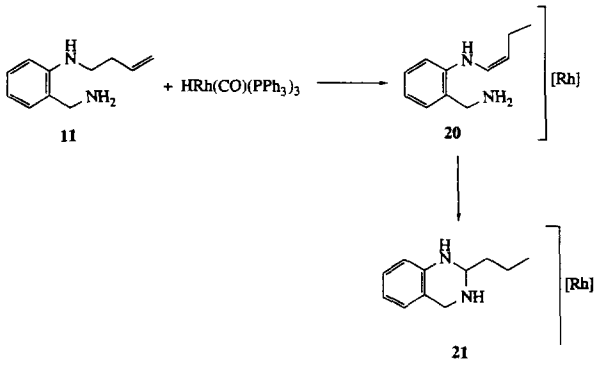


Stoichiometric reaction of the *N*-allylbenzylamine **10** with $HRhCO(PPh_3)_3$ gave a very fast conversion to the oxazine complex **19**.



No evidence for any intermediate isomerised alkene was observed. Comparison with the rhodium-catalysed reaction of this compound with H_2/CO followed the general trend—that stoichiometric reactions lead to less allylic cleavage than catalytic reactions.

One butenyl compound **11** was reacted, the homologue of the *N*-allylaminobenzylamine **1**. Isomerisation to the intermediate *cis*-enamine **20** occurred rapidly followed by cyclisation to the propylquinazoline complex **21**.



11 20 21

No evidence for any other alkenes was obtained. Formation of **21** closely parallels the formation of the ethylquinazoline complex **13** from **1** or **2**.

In conclusion, the unsaturated amines appear to exclusively coordinate to $[Rh(CO)_2Cl]_2$ through nitrogen with no evidence for alkene coordination. In contrast, the products arising from their reaction with $HRh(CO)(PPh_3)_3$ all involve double bond isomerisation which of necessity involves alkene coordination to rhodium. The high regioselectivity observed in most of the rhodium-catalysed reactions of these substrates with H_2/CO must involve coordination of the rhodium catalyst with at least one nitrogen as well as the alkene [1]. A further difference between the catalytic and stoichiometric reactions is that allylic cleavage in both *O*- and *N*-allyl substrates occurs more readily in the catalytic reactions.

3. Experimental section

3.1. General

Infrared (IR) spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. Proton (^1H) and carbon (^{13}C) magnetic resonance spectra were recorded on a Bruker AC-200 or Bruker DRX-400 spectrometer using Me_4Si as the internal standard in $CDCl_3$ or in d_6-benzene for reactions involving $HRh(CO)(PPh_3)_3$. Mass spectra (EI) were obtained on a VG TRIO-1 mass spectrometer at 70 eV. High resolution mass spectra (HRMS) were recorded on a VGF Micromass 7070F spectrometer by peak matching with an internal standard. Elemental analyses were carried out by NAL Pty Ltd, Melbourne, or CMAS, Melbourne.

All manipulations were carried out under a nitrogen atmosphere. All solvents were dried and distilled prior to use. $[Rh(CO)_2Cl]_2$ and $HRh(CO)(PPh_3)_3$ were prepared from $RhCl_3 \cdot 3H_2O$ by literature methods [13,14].

The amine substrates used in this work have all been described previously [1,2,4].

3.2. Reactions of the alkenes 1–4 with $[Rh(CO)_2Cl]_2$

3.2.1. [2-Prop-2'-enylamino)benzylamine]dicarbonylrhodium(I) chloride 5

2-(Prop-2'-enylamino)benzylamine **1** (60 mg, 0.37 mmol) in hexane (5 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (70 mg, 0.18 mmol) in hexane (10 ml) to give an instant red-orange precipitate following the method of Krafft and Wilson [5]. The mixture was stirred at 25 °C for 1 h and filtered to give the complex **5** as a red-orange solid (110 mg, 84%), m.p. 92–94 °C. Anal. Found: C, 40.4; H, 4.1; N, 7.9. $C_{12}H_{14}ClN_2O_2Rh$. Calc: C, 40.4; H, 4.0; N, 7.9%. IR (CCl_4 solution) 2089s, 2028s, 1605m, 1582m, 1557m, 1306m, 1255m, 1154m, 987m, 924w cm^{-1}. ^1H NMR (200 MHz): δ 3.56 (bs, 2H, NH_2); 3.83 (bd, 2H, $J = 3.3$ Hz, H1'); 3.99 (s, 2H, CH_2NH_2); 4.28 (bs, 1H, NH); 5.20 (bdd, 1H, $J = 10.2$, $J = 1.3$ Hz, $H3'_E$); 5.29 (bdd, 1H, $J = 17.2$, $J = 1.3$ Hz, $H3'_Z$); 5.99 (bddt, 1H, $J = 17.2$, $J = 10.2$, $J = 5.5$ Hz, H2); 6.71–6.80 (m, 2H, H3,5); 7.12 (dd, 1H, $J = 7.3$, $J = 1.3$ Hz, H6); 7.25 (td, 1H, $J = 7.9$, $J = 1.5$ Hz, H4). ^{13}C NMR (50 MHz): δ 46.77 (C1', CH_2NH_2); 112.79 (C3); 117.02 (C3'); 118.53 (C5); 122.82 (C1); 130.03, 130.25 (C4,6); 134.67 (C2'); 145.37 (C2). MS (EI): *m/z* (no M^+), 230(2%), 213(2), 160(55), 159(100), 144(30), 133(28), 118(72), 106(55), 104(77), 91(33), 78(45), 77(54), 65(21), 51(41).

3.2.2. [2-Amino-N-(prop-2'-enyl)benzylamine]dicarbonylrhodium(I) chloride 6

In an analogous manner, 2-amino-*N*-(prop-2'-enyl)benzylamine **2** (60 mg, 0.37 mmol) in hexane (5 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (70 mg, 0.18 mmol) in hexane (10 ml) to give an instant canary yellow precipitate. The precipitate was collected by filtration and washed well with hexane to give the complex **6** as a canary yellow solid (90 mg, 69%), m.p. 225–226 °C (dec.). Attempts to obtain a correct microanalysis for the structure were unsuccessful as the compound readily decomposed. IR: (CCl_4 solution) 2088s, 2073s, 2020s, 1999s, 1654m, 1618s, 1560m, 1498m, 1458m, 1246w, 1159w, 991w, 933w cm^{-1}. ^1H NMR (200 MHz): δ 3.40 (bd, 2H, $J \simeq 6.6$ Hz, H1'); 4.02 (bs, 1H, NH); 4.07 (s, 2H, CH_2NH); 5.28–5.37 (m, 2H, H3'); 5.92–6.01 (m, 1H, H2'); 6.94 (t, 1H, $J = 7.6$ Hz, ArH); 7.12 (m, 3H, ArH). ^{13}C NMR (50 MHz): δ 53.30 (C1', CH_2NH); 115.50 (C3'); 117.05, 120.19 (ArCH); 121.89 (C1); 123.63, 129.11 (ArCH); 136.72 (C2'); 145.87 (C2). MS (EI): *m/z* (no M^+); 236(1%), 213(1),

188(4), 173(4), 159(57), 133(61), 118(43), 106(100), 104(68), 91(22), 78(47), 77(65), 65(20), 57(28).

3.2.3. [2-(Prop-2'-enylamino)benzamide]dicarbonylrhodium(I) chloride 7

A solution of 2-(prop-2'-enylamino)benzamide **3** (40 mg, 0.23 mmol) in ethyl acetate (5 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (47 mg, 0.12 mmol) in hexane (10 ml). The mixture was stirred for 1 h and the precipitate collected by filtration to give the complex **7** as a red-orange solid (65 mg, 76%), m.p. 125–127 °C. Anal. Found: C, 39.0; H, 3.3; N, 7.4. $C_{12}H_{12}ClN_2O_3Rh$. Calc.: C, 38.9; H, 3.3; N, 7.6%. IR: ($CDCl_3$ solution) 2068s, 1996s, 1641s, 1599w, 1560m, 1508m cm^{-1}. ^1H NMR (200 MHz): δ 3.83 (bs, 2H, H1'); 5.14 (bdd, 1H, $J = 10.2$, $J = 1.4$ Hz, $H3'_E$); 5.27 (bdd, 1H, $J = 17.2$, $J = 1.5$ Hz, $H3'_Z$); 5.84–6.03 (m, 1H, H2'); 6.55–6.68 (m, 2H, H3,5); 7.28 (td, 1H, $J = 8.5$, $J = 1.5$ Hz, H4); 7.53 (dd, 1H, $J = 7.9$, $J = 1.4$ Hz, H6); 8.11 (bs, 1H, NH). ^{13}C NMR (50 MHz): δ 44.63 (C1'); 111.14 (C3); 113.17 (C1); 113.83 (C5); 115.04 (C3'); 128.31, 132.30 (C4,6); 134.29 (C2'); 149.33 (C2); 171.79 (C=O).

3.2.4. [2-(Prop-2'-enyloxy)benzylamine]dicarbonylrhodium(I) chloride 8

2-(Prop-2'-enyloxy)benzylamine **4** (60 mg, 0.37 mmol) in hexane (4 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (70 mg, 0.18 mmol) in hexane (10 ml) to give an instant blood red precipitate. The reaction was stirred for a further 1 h and the solvent removed in vacuo and the residue passed down a silica column in ethyl acetate to remove any unreacted amine. Removal of the solvent under reduced pressure gave **8** as red-green crystals (70 mg, 53%), m.p. 96–97 °C. Anal. Found: C, 40.4; H, 3.7; N, 4.0. $C_{12}H_{13}ClNO_3Rh$. Calc.: C, 40.3; H, 3.7; N, 3.9%. IR: ($CDCl_3$ solution) 3292m, 3213m, 2084s, 2007s, 1602m, 1493m, 1455m, 1244s, 1162m, 996m, 910m, 758m, 733s cm^{-1}. ^1H NMR (200 MHz); δ 3.51 (bs, 2H, NH_2); 4.06 (bt, 2H, $J = 7.0$ Hz, CH_2NH_2); 4.62 (dt, 2H, $J = 5.4$, $J = 1.3$ Hz, H1'); 5.32–5.47 (m, 2H, H3'); 6.00–6.19 (m, 1H, H2'); 6.90–7.00 (m, 2H, H3, 5); 7.21–7.38 (m, 2H, H4,6). ^{13}C NMR (50 MHz): δ 47.59 (CH_2NH_2); 69.06 (C1'); 111.86 (C3); 118.75 (C3'); 121.33 (C5); 125.89 (C1); 130.37, 130.40 (C4,6); 132.42 (C2'); 156.73 (C2). MS (EI): m/z (no M^+), 301(< 1%), 269(1), 247(4), 212(4), 178(4), 162(22), 146(61), 145(61), 122(85), 121(58), 107(42), 95(49), 78(42), 77(100), 66(38), 57(60).

3.3. Reactions of the alkenes 1, 2 and 4–11 with $HRh(CO)(PPh_3)_3$

3.3.1. Reaction of 2-(prop-2'-enylamino)benzylamine 1

A solution of $HRh(CO)(PPh_3)_3$ (84.9 mg, 92.4 μmol) in d_6-benzene (0.5 ml) was syringed into an NMR tube containing a solution of 2-(prop-2'-enylamino)benzylamine **1** (15.0 mg, 92.4 μmol) in d_6-benzene (0.5 ml). The mixture was heated in a water bath at 60 °C and ^1H NMR spectra were recorded at intervals over 1 h. Rapid formation of the rhodium complexes of (*E*)- and (*Z*)-2-(prop-1'-enylamino)benzylamines **12** occurred. ^1H NMR (200 MHz): δ 1.70 (dd, $J = 6.6$, $J = 1.5$ Hz, H3' (*E*)); 1.78 (dd, $J = 6.9$, $J = 1.7$ Hz, H3' (*Z*)); 4.60 (dq, $J = 8.35$, $J = 6.9$ Hz, H2' (*Z*)). After 1 h the starting material was completely converted to a rhodium complex of 2-ethyl-1,2,3,4-tetrahydroquinazoline **13**. IR: (d_6-benzene) 2280s, 1618m, 1479m, 1454m, 1435m, 1330s, 1202w, 1162w, 1119w, 1088w, 812s, 747m, 696m cm^{-1}. ^1H NMR (200 MHz): δ 0.84 (t, 3H, $J = 7.4$ Hz, H2'); 1.12–1.30 (m, 2H, H1'); 3.34 (bs, 1H, NH); 3.57–3.72 (m, 2H, H2,4); 3.93 (dd, 1H, $J_{AB} = 16.7$, $J = 11.1$ Hz, H4); 6.33 (d, 1H, $J = 7.7$ Hz, ArH); 6.67–7.07 (m, ArH); 7.48 (bs, ArH). ^{13}C NMR (50 MHz): δ 9.41 (C2'); 29.66 (C1'); 46.84 (C4); 68.19 (C2); 115.16, 117.82 (ArCH); 122.19 (ArC); 144.50 (C8a).

The solution of the complex **13** was added to a solution of 1,2-bis-diphenylphosphinoethane (dppe) (151 mg, 379 μmol) in benzene (5 ml) and the resulting mixture stirred at 50 °C for 15 min. The solution was concentrated, hexane added, and the resulting pale-yellow precipitate removed by filtration. The filtrate was evaporated to give a mixture of excess dppe and 2-ethyl-1,2,3,4-tetrahydroquinazoline **14**. ^1H and ^{13}C NMR spectral data for **14** was identical to that obtained from an authentic sample of **14** prepared as described previously [15], m.p. 83–84 °C (softens 69 °C) (Ref. [15] 88–90 °C.) ^1H NMR (400 MHz); δ 1.05 (t, 3H, $J = 7.5$ Hz, H2') [1]; 1.63 (m, 2H, H1'); 4.07 (d, 1H, $J_{AB} = 16.7$ Hz, H4); 4.08 (t, 1H, $J = 5.9$ Hz, H2); 4.12 (d, 1H, $J_{AB} = 16.7$ Hz, H4); 6.51 (d, 1H, $J = 8.0$ Hz, H8); 6.66 (td, 1H, $J = 7.4$, $J = 1.0$ Hz, H6); 6.89 (d, 1H, $J = 7.4$ Hz, H5); 7.00 (bt, 1H, $J \simeq 7.6$ Hz, H7). ^{13}C NMR (100 MHz): δ 9.27 (C2'); 29.45 (C1'); 46.61 (C4); 68.12 (C2); 114.95 (C8); 117.93 (C6); 121.67 (C4a); 126.15 (C5); 127.21 (C7); 143.76 (C8a). MS (EI): m/z 162(M^+, 10%), 133(100), 106(56), 77(20).

3.3.2. Reaction of 2-amino-N-(prop-2'-enyl)benzylamine 2

As described above, a solution of $HRh(CO)(PPh_3)_3$ (84.9 mg, 92.4 μmol) in d_6-benzene (0.5 ml) was syringed into an NMR tube containing a solution of 2-amino-*N*-(prop-2'-enyl)benzylamine **2** (15.0 mg, 92.4 μmol) in d_6-benzene (0.5 ml) and the reaction monitored as before. After 1 h at 60 °C complete conversion to the rhodium complex **13** had occurred.

3.3.3. Reaction of 2-(prop-2'-enyloxy)benzylamine 4

As described above, a solution of $HRh(CO)(PPh_3)_3$ (84.9 mg, 92.4 μmol) in d_6-benzene (0.5 ml) was sy-

[1] (^1H NMR: Ref. [15] quotes 0.8 ppm).

ringed into an NMR tube containing a solution of 2-(prop-2′-enyloxy)benzylamine **4** (15.0 mg, 92.4 μmol) in d_6-benzene (0.5 ml) and the reaction monitored by ^{1}H NMR spectroscopy. After 30 min at 60 °C the starting material had been completely consumed to give a mixture of propene and the rhodium complexes **15** and **16** in the ratio of 1:1:1. IR: (d_6-benzene) 2280s, 1617m, 1450m, 1439m, 1330s, 1201m, 1119m, 812s cm^{-1}. ^{1}H NMR (200 MHz); δ 1.37 (dd, J = 6.9, J = 1.6 Hz, H3′-**15**-*E*); 1.53 (dt, J = 6.5, J = 1.6 Hz, H3-propene); 1.64 (dd, J = 6.9, J = 1.7 Hz, H3′-**15**-*Z*); 3.20 (bs) and 3.80 (s) (CH_2NH$_2$ **15** and **16**); 4.63 (apparent p, J = 6.9 Hz, H2′-**15**-*Z*); 4.90–5.05 (m, H1-propene); 5.21 (dq, J = 12.1, J = 6.9 Hz, H2′-**15**-*E*); 5.71 (ddq, J = 17.0, J = 10.0, J = 6.5 Hz, H2-propene).

3.3.4. Reaction of 2-[N-benzyl-N-(prop-2′-enyl)amino]benzylamine 9

A solution of HRh(CO)(PPh$_3$) (69.3 mg, 75.2 mmol) in d_6-benzene (0.5 ml) was syringed into a sealed NMR tube containing **9** (19.0 mg, 75.2 mmol) in d_6-benzene (0.5 ml) and maintained at 60 °C. The ^{1}H NMR spectra showed initial isomerisation to a rhodium complex of 2-[*N*-benzyl-*N*-(prop-1′-enyl)amino]benzylamine **17**. ^{1}H NMR (200 MHz): δ 1.21 (dd, J = 7.03, J = 1.7 Hz, H3′, minor isomer); 1.61 dd, J = 6.6, J = 1.5 Hz, H3′, major isomer); 3.61 (bs, CH_2NH$_2$); 4.33 (s, CH_2Ph) followed by formation of the rhodium complex of 1-benzyl-2-ethyl-1,2,3,4-tetrahydroquinazoline **18**. ^{1}H NMR (200 MHz): δ 0.85 (t, 3H, J = 7.3 Hz, H2′); 1.47 (m, 2H, H1′); 3.57–3.92 (m, 3H, H2,4); 4.10 (d, 2H, J = 2.1 Hz, CH_2Ph); 6.47 (d, 1H, J = 8.0 Hz, ArH); 6.63–7.78 (m, ArH). ^{13}C NMR (50 MHz): δ 10.05 (C2′); 25.44 (C1′) 42.92 (C4); 53.04 (*C*H$_2$Ph); 74.42 (C2); 112.61 (C8); 116.50 (C6); 122.34 (C4a); 140.01 (ArC); 144.55 (C8a).

The free quinazoline, 1-benzyl-2-ethyl-1,2,3,4-tetrahydroquinazoline was isolated by preparative chromatography of the rhodium complex **18** on silica (20% EtOAc–light petroleum) as a viscous oil whose NMR data were identical to those of an authentic sample prepared from propanal (82 mg, 1.41 mmol) and 2-(benzylamino)benzylamine (0.3 g, 1.41 mmol) [15] as a viscous oil (0.33 g, 92%). EI-HRMS: Found m/z (M$^+$) 252.162 ± 0.003. $C_{17}H_{20}N_2$. Calc.: 252.163. IR: 3316w, 3063w, 3028w, 2930s, 2854m, 1603s, 1501s, 1464m, 1451s, 1346m, 1290m, 1252m, 1098m, 957m, 744s, 698m cm^{-1}. ^{1}H NMR (400 MHz): δ 1.03 (t, 3H, J = 7.4 Hz, H2′); 1.76 (m, 2H, H1′); 2.27 (bs, 1H, NH); 3.98 (d, 1H, J_{AB} = 16.7 Hz, H4); 4.13 (d, 1H, J_{AB} = 16.7 Hz, H4); 4.17 (dd, 1H, J = 7.8, J = 5.8 Hz, H2); 4.48, (d, 1H, J_{AB} = 17.2 Hz, (CH_2Ph); 4.56 (d, 1H, J_{AB} = 17.2 Hz, CH_2Ph); 6.54 (d, 1H, J = 8.2 Hz, H8); 6.69 (td, 1H, J = 7.3, J = 0.9 Hz, H6); 6.99 (d, 1H, J = 7.3 Hz, H5); 7.05 (td, 1H, J = 8.2, J = 1.5 Hz, H7); 7.30–7.40 (m, 5H, ArH). ^{13}C NMR (100 MHz): δ 9.77 (C2′); 25.02 (C1′); 42.50 (C4); 52.90 (*C*H$_2$Ph); 73.96 (C2); 112.22 (C8); 116.06 (C6); 121.52 (C4a); 125.48, 126.35, 126.73, 127.51, 128.49 (C5, 7, ArCH); 139.10 (ArC); 143.84 (C8a). MS (EI): m/z 252(M$^+$, 6%), 224(9), 223(60), 196(11), 195(18), 194(30), 131(15), 118(30), 91(100), 77(10).

3.3.5. Reaction of 2-[N-(prop-2′-enyl)aminomethyl]phenol 10

Following the procedure described previously, a solution of HRh(CO)(PPh$_3$)$_3$ (84.9 mg, 92.4 μmol) in d_6-benzene (0.5 ml) was syringed into an NMR tube containing a solution of 2-[*N*-(prop-2′-enyl)aminomethyl]phenol **10** (15.0 mg, 92.4 μmol) in d_6-benzene (0.5 ml) and the reaction monitored by ^{1}H NMR spectroscopy. Analysis of the reaction mixture after 10 min at 60 °C indicated the reaction had given a rhodium complex of 2-ethyl-2,3-dihydro-4*H*-1,3-benzoxazine **19**. IR: (d_6-benzene) 2280s, 1618m, 1453m, 1436m, 1330s, 812s, 696m cm^{-1}. ^{1}H NMR (200 MHz): δ 0.93 (t, 3H, J = 7.5 Hz, H2′); 1.42–1.79 (m, 2H, H1′); 3.40 (dd, 1H, J_{AB} = 16.7, J = 4.5 Hz, H4); 3.80 (dd, 1H, J_{AB} = 16.7, J = 10.5 Hz, H4); 4.37 (dt, 1H, J = 12.7, J = 5.9 Hz, H2); 6.54–7.09 (m, ArH); 7.48 (bs) and 7.64 (m) (ArH). ^{13}C NMR (50 MHz): δ 9.23 (C2′); 28.79 (C1′); 44.51 (C4); 88.47 (C2); 117.32, 120.09 (ArCH); 122.58 (C4a).

An authentic sample of the free benzoxazine, 2-ethyl-3,4-dihydro-2*H*-1,3-benzoxazine was prepared from 2-(aminomethyl)phenol (0.25 g, 2.03 mmol) and propanal (0.47 g, 8.12 mmol) using the method of McDonagh and Smith [16] as a clear liquid (0.25 g, 75%). B.p. (oven) 75 °C/0.1 mmHg. Anal. Found: 163.100 ± 0.001. $C_{10}H_{13}NO$. Calc.: 163.100. IR: 3318m, 2968s, 2937s, 2879s, 1644w, 1609m, 1585s, 1488s, 1457s, 1384m, 1248s, 1223s, 1032m, 970m, 919s, 753s, 665w cm^{-1}. ^{1}H NMR (400 MHz): δ 1.06 (t, 3H, J = 7.5 Hz, H2′); 1.69–1.86 (m, 2H, H1′); 3.90 (d, 1H, J_{AB} = 16.9 Hz, H4); 4.13 (d, 1H, J_{AB} = 16.9 Hz, H4); 4.65 (t, 1H, J = 5.7 Hz, H2); 6.77 (d, 1H, J = 8.2 Hz, H8); 6.82 (td, 1H, J = 7.4, J = 1.7 Hz, H6); 6.92 (d, 1H, J = 7.3 Hz, H5); 7.09 (td, 1H, J = 7.7, J = 1.6 Hz, H7). ^{13}C NMR (100 MHz): δ 8.90 (C2′); 28.39 (C1′); 44.31 (C4); 88.26 (C2); 116.92 (C8); 120.05 (C6); 121.99 (C4a); 126.12 (C5); 127.62 (C7); 154.63 (C8a). Mass spectrum: m/z 163 (M$^+$, 42%), 148(7), 134(36), 107(100), 78(41), 77(47), 57(52).

3.3.6. Reaction of 2-(but-3′-enylamino)benzylamine 11

A solution of HRh(CO)(PPh$_3$)$_3$ (104.1 mg, 11.3 mmol) in d_6-benzene (0.75 ml) was syringed into a sealed NMR tube containing 2-(but-3′-enylamino)benzylamine) **11** (20.0 mg, 11.3 mmol) in d_6-benzene (0.25 ml) and spectra were recorded of the solution at

60 °C. Isomerisation to the rhodium complex **20** was first observed, ^{1}H NMR (200 MHz): δ 1.12 (t, 3H, J = 7.5 Hz, H4′); 2.27 (m, 2H, H3′); 4.57 (apparent q, 1H, J = 8.4 Hz, H2′), followed by conversion to the rhodium complex of 2-propyl-1,2,3,4-tetrahydroquinazoline **21**. ^{1}H NMR (200 MHz): δ 0.83 (m, 3H, H3′); 1.11 (m, 4H, H1′, 2′); 3.32 (bs, 1H, NH); 3.62 (dd, 1H, J_{AB} = 16.8, J = 5.1 Hz, H4); 3.76 (m, 1H, H2); 3.93 (dd, 1H, J_{AB} = 16.8, J = 11.4 Hz, H4); 6.35 (d, 1H, J = 8.1 Hz, H8); 6.65–8.11 (m, ArH). ^{13}C NMR (50 MHz): δ 14.27 (C3′); 18.44 (C2′); 39.00 (C1′); 46.87 (C4); 66.78 (C2); 115.19, 117.85 (C6,8); 144.48 (C8a).

A sample of the free quinazoline, 2-propyl-1,2,3,4-tetrahydroquinazoline was prepared as described above [15] from butanal (0.29 g, 4.07 mmol) and 2-aminobenzylamine (0.50 g, 4.07 mmol). Recrystallisation from light petroleum gave yellow crystals (0.45 g, 63%) m.p. 55.7–56.5 °C. Sublimation (72 °C/0.03 mmHg) gave an analytical sample. Anal. Found: C, 75.3; H, 9.0; N, 15.9. $C_{11}H_{16}N_2$. Calc.: C, 75.0; H, 9.2; N, 15.9%. IR: 3287bm, 1609m, 1589w, 1404m, 1300w, 1251w, 1138w, 815w, 744m cm^{-1}. ^{1}H NMR (200 MHz): δ 0.98 (m, 3H, H3′); 1.54 (m, 5H, H1′, 2′, NH); 3.94 (d, 1H, J_{AB} = 16.8 Hz, H4); 4.12 (d, 1H, J_{AB} = 16.8 Hz, H4); 4.14 (t, 1H, J = 5.7 Hz, H2); 6.50 (dd, 1H, J = 7.9, J = 1.0 Hz, H8); 6.67 (td, 1H, J = 7.4, J = 1.2 Hz, H6); 6.94 (m, 1H, H5); 7.04 (m, 1H, H7). ^{13}C NMR (50 MHz): δ 14.03 (C3′); 18.16 (C2′); 38.58 (C1′); 46.37 (C4); 66.34 (C2); 114.87, 117.91 (C6,8); 121.54 (C4a); 126.09, 127.10 (C5,7), 143.59 (C8a). MS (EI): m/z 176(M^+, 8%), 134(15), 133(100), 131(13), 106(80), 104(13), 78(12), 77(25), 66(12).

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