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Comparison of a range of rhodium-based catalysts for the hydroformylation of selected alkenes

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Abstract

Four rhodium-based catalyst systems $(OC)_4\overline{W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)}$ **1**, $(OC)_2\overline{RhMo(CO)_3(C_5H_4PPh_2)}$ **2**, $(OC)_2\overline{RhW(CO)_3(C_5H_4PPh_2)}$ **3**, and $[Rh(OAc)_2]_2/PPh_3$ have been used in the hydroformylation of 1-hexene, styrene and some phosphino-, amino- and amido-alkenes. In general the catalysts showed very similar reactivity and selectivity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; Rhodium catalysts; Bimetallic catalysts

1. Introduction

Hydroformylation of alkenes has been carried out for many years mainly using mononuclear, homogeneous catalysts [1,2]. The use of bimetallic catalysts, both homo- and heterobimetallic, has been studied more recently [3].

A good deal of work has been focused on the development of heterobimetallic catalysts in the hope that the presence of two different adjacent metal centres might lead to increased catalytic activity with enhanced chemo- and regioselectivity [4–7]. A general problem associated with the use of bi- or polymetallic catalysts is their tendency to degrade to monometallic species under the reaction conditions [8]. Various strategies have been adopted to overcome this problem including the use of bridging dithiolato [9] or bridging diphosphido ligands [10]. Strong evidence for the retention of the bimetallic system during the catalytic cycle has been provided, at least for the phosphido-bridged heterobimetallic rhodium catalysts [11]. Although there have been some claims as to the enhanced

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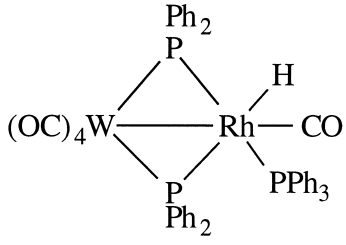
activity and selectivity of bimetallic catalysts versus their monometallic counterparts [12–18], no systematic comparison using a variety of substrates appears to have been carried out.

In this paper we describe a comparison of the results obtained on hydroformylation of 1-hexene, styrene and a range of amino- and phosphino-alkenes using three heterobimetallic catalysts and a rhodium only catalyst system, $[Rh(OAc)_2]_2/PPh_3$ with a P/Rh ratio of 2/1 which we have used previously, e.g., Ref. [10]. It has been shown that the rhodium-catalysed reactions of unsaturated amines with H_2/CO can exhibit significant differences in both chemo- and regioselectivity depending on the catalyst and the reaction conditions [19–21]. Reactions of the phosphinoalkenes can also show chemoselectivity in that the initially formed aldehydes are further reduced to alcohols when some catalyst systems are used [22]. These substrates were thus considered good candidates for the comparison of catalytic systems. In addition, it has been shown that reactions of unsaturated amides show significant differences in product ratios with varying catalyst systems and thus reactions of an amide, *N*-methyl-*N*-benzylpent-4-enamide [23,24] were also investigated using the above catalyst systems.

2. Results and discussion

2.1. Catalyst preparation

The heterobimetallic rhodium compounds chosen for study in these hydroformylation reactions were the established phosphido-bridged tungsten-rhodium compound **1** [25] and the cyclopentadienylphosphine complexes **2** and **3**. The latter compounds were made by the method described by Casey et al. [26] but their potential catalytic activity does not appear to have been explored. The molybdenum compound **2** was prepared in 44% overall yield and the tungsten compound **3** in 37% yield from the sequential reaction of $(CH_3CN)_3M(CO)_3$ with $Li(C_5H_4PPh_2)$ and $[Rh(CO)_2Cl]_2$. It was observed that, in contrast to the 4 h required for preparation of the reagent $(CH_3CN)_3Mo(CO)_3$, the tungsten analogue required prolonged reflux (120 h).



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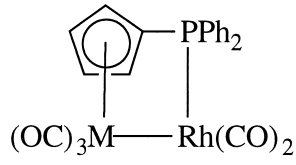


2; M=Mo, **3**; M=W

2.2. Catalytic reactions with styrene and 1-hexene

Reactions of styrene with H_2/CO (1:1, 400 psi, 2.76 MPa) for 20 h at 50°C were carried out using $[Rh(OAc)_2]_2/PPh_3$, $HRh(CO)(PPh_3)_3$, and the bimetallic catalysts **1**, **2** and **3**. All reactions gave complete conversion to a mixture of the branched and linear aldehydes in a ratio 96:4 (± 2). These

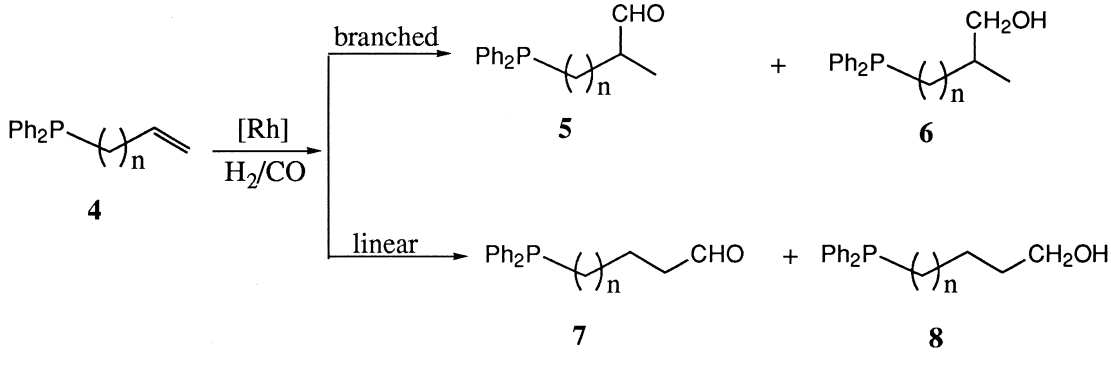
ratios are identical to those reported previously for reactions of styrene under similar conditions using mono [27] and bimetallic [28] catalysts. It was thought that the steric requirements around the Rh atom in the phosphido-bridged complex **1** may be less than in $HRh(CO)(PPh_3)_3$ due to the ligand phosphorus atoms being pulled back into the bridge (ring) system, but no increase in the percentage of branched aldehyde was observed. The cyclopentadienylphosphine complexes **2** and **3** also appear to have reduced steric requirements relative to $HRh(CO)(PPh_3)_3$ but again no significant change in regioselectivity was observed.

The hydroformylation of unsubstituted 1-alkenes generally favours linear aldehyde formation [1]. Reactions of 1-hexene with H_2/CO (1:1, 400 psi, 2.76 MPa) for 20 h at 60°C using $[Rh(OAc)_2]_2/PPh_3$ and the bimetallic catalysts **2** and **3** resulted in complete conversion to a mixture of linear and branched aldehydes. There was only a small variation in regioselectivity from 60:40 for $[Rh(OAc)_2]_2/PPh_3$ to 70:30 for complex **3**.

The possibility that these reactions involved breakdown of the heterobimetallic complexes and catalysis by a monomeric rhodium species thus had to be considered. Evidence for retention of the metal–metal bond in the phosphido-bridged species **1** has been discussed previously [11]. A reaction of 1-hexene using the cyclopentadienylphosphine complex **3** as a catalyst was carried out in which the ratio of substrate to catalyst was 4:1. After removal of C7-aldehydes the residue was analysed by ^1H and ^{31}P NMR and IR spectroscopy. The ^{31}P NMR was similar to that recorded for **3** and showed the satellites associated with W–Rh–P coupling. Full identification of the compound after reaction was not possible. Although the ^1H as well as the ^{31}P NMR spectrum was very similar to that of **3**, the IR spectrum showed interesting changes in the region associated with Rh–CO stretching frequencies.

2.3. Catalytic reactions of phosphinoalkenes

The phosphinoalkenes **4**; $n = 1$, 2 and 3 were reacted with H_2/CO at 80°C for 20 h in the presence of the cyclopentadienylphosphine compounds **2** and **3** and the results compared with published data for the bimetallic complex **1** [10,11] and $[Rh(OAc)_2]_2$ [22]. (Table 1).



Reactions of the phosphinoalkene **4**; $n = 2$ were regiospecific in all cases. Reactions at 80°C led to further reduction of the initially formed aldehyde **5**; $n = 2$ to the alcohol **6**; $n = 2$. The reduction was complete in all cases except for the reaction using the W–Rh cyclopentadienylphosphine complex **3**, which gave almost equal amounts of aldehyde and alcohol. Reactions using $[Rh(OAc)_2]_2$ at lower temperatures also gave varying amounts of aldehyde [22].

Table 1
Reactions of phosphinoalkenes **4**[a]

Catalyst system	Reactant **4**	Product ratios			
		5:	**6**:	**7**:	**8**
$[Rh(OAc)_2]_2/PPh_3$	$n=1$	–	30	–	20[b]
1	$n=1$	–	36	–	18[c]
2	$n=1$	–	28	–	30[d]
3	$n=1$	13	–	18	–[e]
$[Rh(OAc)_2]_2/PPh_3$	$n=2$	–	100 (86%)	–	–
1	$n=2$	–	100 (77%)	–	–
2	$n=2$	–	100 (79%)	–	–
3	$n=2$	57	43	–	–
$[Rh(OAc)_2]_2/PPh_3$	$n=3$			[f]	
1	$n=3$	94	17	6	–
2	$n=3$	100 (89%)	–	–	–
3	$n=3$	100	–	–	–

[a] Reactions with H_2/CO, 1:1 (400 psi, 2.76 MPa) at 80°C for 20 h with a 1:100 Rh:substrate ratio. Product ratios determined from ^1H NMR spectra; isolated yields of products in parenthesis. Each reaction has been carried out at least twice. Variation in yields and product ratios were $\leq 3\%$ except for reaction of **4**; $n=3$ with $[Rh(OAc)_2]_2/PPh_3$.
[b] 50% starting material.
[c] 46% starting material.
[d] 42% starting material.
[e] 69% starting material.
[f] 13–50% of $Ph_2P(CH_2)_4CH_3$ formed. Branched and linear products each a mixture of aldehydes and alcohols, branched:linear ratio 85:15 (± 5).

The reaction of the phosphinoalkene **4**; $n=3$ using the Mo–Rh cyclopentadienylphosphine **2** was highly chemo- and regioselective giving only the branched-chain aldehyde **5**; $n=3$, a pure sample of which was obtained in high yield (89%). This selectivity for branched aldehyde formation was also displayed by the W–Rh cyclopentadienylphosphine complex **3**. These catalysts are thus superior in that the $[Rh(OAc)_2]_2/PPh_3$ system gave significant amounts of double bond saturation and the tungsten–rhodium phosphido-bridged catalyst **1** was not regiospecific leading to the formation of about 6% linear aldehyde [10].

Reactions of the allylic phosphine **4**; $n=1$ have been shown previously to be significantly slower than their longer chain homologues [11,22]. This trend was again confirmed in reactions of the allylic phosphine using the Mo–Rh cyclopentadienylphosphine **2** and the related W–Rh compound **3** as catalyst which gave only 60 and 30% conversions, respectively, under the standard conditions. This reaction also showed poor regioselectivity giving an approximately 50:50 ratio of the alcohols **6**; $n=1$ and **8**; $n=1$ for the Mo–Rh compound possibly for reasons suggested previously [11]. The corresponding W–Rh compound **3** surprisingly gave the aldehydes **5**; $n=1$ and **7**; $n=1$ again with poor regioselectivity.

*2.4. Catalytic reactions of N-benzyl and N-(1-phenylethyl)pent-4-enylamine **9***

Zhang and Ojima have demonstrated that the regioselectivity of reactions of *N*-benzylpent-4-enylamine **9a** is sensitive to reaction conditions. Very high regioselectivities for formation of either the 3-methylpiperidine **14a** or the azepane **15a** can be achieved using $HRh(CO)(PPh_3)_3$ with varying amounts of added phosphine ligand [21]. Formation of **14** and **15** involves cyclisation of the initially

Table 2
Reactions of *N*-benzylpent-4-enamine **9a** with H_2/CO[a]

Entry no.	Catalyst system	*T* (°C)	Product ratios[b]				
			12:	**13**:	**14**:	**15**:	**17**
1	$[Rh(OAc)_2]_2/PPh_3$	60	28	19	10	22	21
2	$[Rh(OAc)_2]_2$/BIPHEPHOS	60	–[c]	40	–	20	40
3	**1**	60	29	–	12	59	–
4	**1**	40	27	16	–	21	15[d]
5	**2**	60	20	17	–	–	15[e]
6	**3**	60	19	16	–	13	12[f]

[a] Reactions for 20 h with H_2/CO (400 psi, 2.76 MPa).
[b] Based on integrals from ^1H NMR spectra of the total product.
[c] Implies < 5% of compound detected by ^1H NMR or GLC.
[d] 21% starting material.
[e] 48% starting material.
[f] 39% starting material.

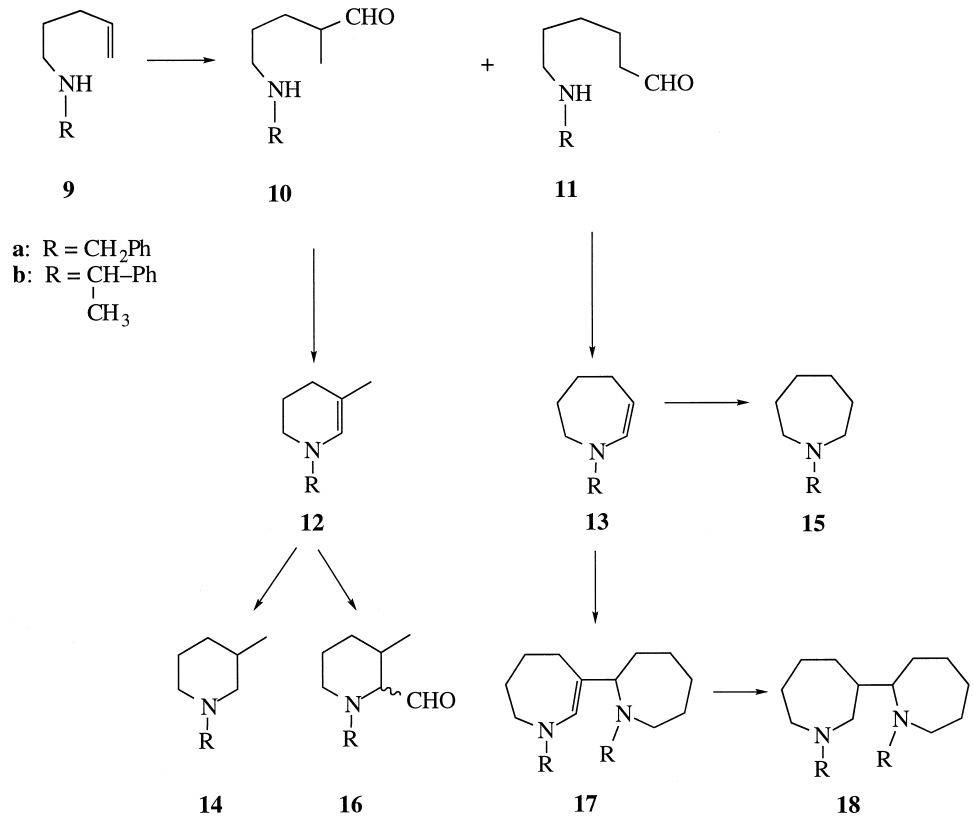
formed branched **10** and linear **11** aldehydes to form the cyclic enamines **12** and **13** which are subsequently hydrogenated under the relatively severe reaction conditions of 100°C and 1800 psi, 12.40 MPa of H_2/CO. In order to allow for maximum discrimination, we have reacted both the benzyl and *N*-(1-phenylethyl)pentenylamines **9** with H_2/CO in the presence of the four catalyst systems $[Rh(OAc)_2]_2/PPh_3$, **1**, **2**, and **3** under milder conditions. Reactions of the *N*-benzyl compound **9a** are summarised in Table 2 and of the *N*-(1-phenylethyl) compound **9b** in Table 3.

The products were identified by ^1H NMR spectroscopy and GLC involving comparisons with literature data and/or with authentic samples except for the enamine **13** and its dimerisation product **17**. The structures of **13** and **17** were inferred from spectral data and by hydrogenation to the saturated heterocycles **15** and **18**. Product ratios are based on integration of ^1H NMR spectra as it proved very difficult to achieve GLC separation of the regioisomers **12**/**13** and **14**/**15** (Scheme 1).

Table 3
Reactions of *N*-1-phenylethylpent-4-enamine **9b** with H_2/CO

Entry no.	Catalyst system	*T* (°C)	Time (h)	*P*[a] (psi)	Product ratios[b]					
					12:	**13**:	**14**:	**15**:	**16**:	**17**
7	$Rh[OAc)_2]_2/PPh_3$	80	20	1200	39	34	–[c]	–	–	27
8	$Rh[OAc)_2]_2/PPh_3$	80	20	1500	35	27	12	–	–	26
9	$Rh[OAc)_2]_2/PPh_3$	80	20	400	32	–	–	37	–	31
10	$HRh(CO)(PPh_3)_3$	80	60	1500	28	–	–	40	12	–[d]
11	$HRh(CO)(PPh_3)_3$	80	60	1500	27	–	–	63	–	10
12	$[Rh(OAc)_2]_2$/BIPHEPHOS	80	20	1200	14	38	–	15	–	33
13	$[Rh(OAc)_2]_2$/BIPHEPHOS	60	20	400	5	49	–	–	–	46
14	**1**	80	20	400	39	–	–	40	–	21
15	**2**	80	20	400	34	18	13	18	–	17
16	**3**	80	20	400	20	–	7	63	–	–[e]

[a] 400, 1200 and 1500 psi are equivalent to 2.76, 8.28 and 10.34 MPa.
[b] Based on integrals from ^1H NMR spectra of the total product.
[c] Implies < 5% of compound detected by ^1H NMR or GLC.
[d] 20% of the linear aldehyde **11b** was observed.
[e] 10% starting material.



Scheme 1.

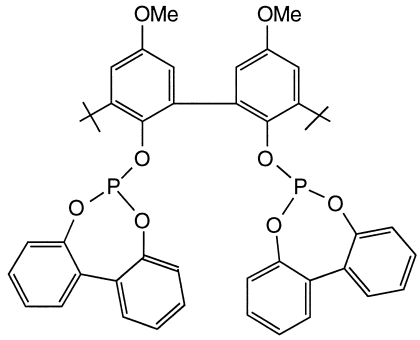
*2.4.1. Reactions of N-benzylpent-4-enylamine **9a***

Reactions of **9a** with H_2/CO at 60°C gave good conversions to products with the exception of the cyclopentadienylphosphine complexes **2** and **3** which gave 40–50% of recovered starting material. The products in all cases, except reaction 2 using the bulky BIPHEPHOS ligand, were a mixture of the 6- and 7-membered cyclic enamines **12a** and **13a**, their saturated analogues **14a** and **15a** and the dimeric material **17a** arising from self-condensation of the enamine **13a**. Only the dimer arising from the 7-ring enamine **13a** was detected. Specificity in enamine dimerisation has been previously noted where mixtures of 5- and 6-membered enamines only led to cross-coupled products [20]. The reactivity of these cyclic enamines has been well established [29,30]. Although the fates of the intermediate enamines varied with catalyst (cf. reactions 1, 3, 5 and 6) the overall regioselectivity for the branched to linear products **10** and **11** varied little. Thus, when the percentages of (**12a** + **14a**) vs. (**13a** + **15a** + 2 × **17a**) were compared, the regioselectivities varied only from 40:60 for reaction 3 to 30:70 for reactions 1, 4, 5 and 6. These ratios, which are typical of those obtained from reactions of 1-alkenes, show that no chelation control of selectivity by the amine nitrogen is occurring and suggest that all catalyst centres are of comparable size. The ability of the different catalysts to hydrogenate the intermediate enamines differed markedly. No hydrogenation occurred with the cyclopentadienylphosphine compound **2** (reaction 5) and in contrast a majority of the product was saturated when the phosphido-bridged compound **1** was used (reaction 3). Other catalysts gave intermediate degrees of enamine hydrogenations in the range 18% (reaction 6) to 26% (reaction 1). The results tentatively suggest that bimetallic W–Rh complexes, e.g., **1** and **3**, are more likely to promote enamine

hydrogenation than the Mo–Rh compound **2** although the $[Rh(OAc)_2]_2/PPh_3$ system promoted hydrogenation to a similar degree. It is of interest that this variation appears to be generally associated with hydrogenation of the seven-membered enamine **13**, e.g., in reaction 3 all of **13** had been hydrogenated to give **15** whereas only 29% of **12** had been converted into its saturated analogue **14**. None of the catalysts led to hydrogenation of the alkene in the starting material.

A reaction using the W–Rh compound **1** at 40°C gave significantly less saturated material (reaction 4) and a concurrent formation of dimeric material.

A reaction was carried out using the bulky, bidentate phosphite ligand BIPHEPHOS [19,31] which was highly regioselective giving less than 5% of materials derived from the branched aldehyde **10**.



BIPHEPHOS

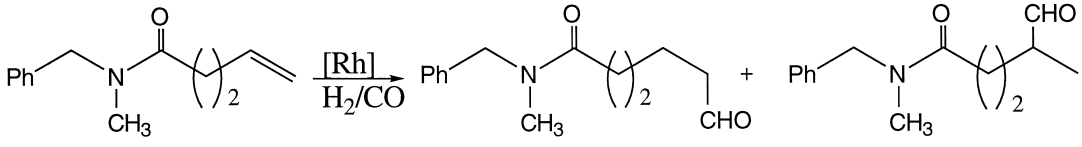
*2.4.2. Reactions of N-(1-phenylethyl)pent-4-enylamine **9b***

Reactions of the homologue **9b** of the benzyl compound **9a** were carried out under a variety of conditions. A reaction using BIPHEPHOS as ligand (reaction 13) gave a very similar result to that of the benzyl compound **9a** under identical conditions (reaction 2). Again, the products mainly arose from a highly regioselective linear hydroformylation, the only difference being that no hydrogenated material **15b** was observed. Some hydrogenation occurred during a reaction at 80°C (reaction 12).

Other reactions were carried out at 80°C in order to make comparisons with the reactions of the unsaturated phosphines (see Table 1). All reactions went to completion at this temperature with the exception of reaction 16 using the W–Rh cyclopentadienylphosphine compound **3**. This compound was one of the less active catalysts in reactions of the benzyl homologue **9a** (see Table 2). The reactions all showed products originating from an initial hydroformylation with about 30:70 branched to linear regioselectivity (reactions 9, 14, 15 and 16). All showed the presence of significant amounts of at least one of the unsaturated products **12b**, **13b** and **17b**. However, the ease of hydrogenation of the intermediate enamines **12** and **13**, R = $CH(CH_3)Ph$ showed very different variations with catalyst to those displayed in reactions of the benzyl analogue **9a**. Thus, e.g. the Mo–Rh catalyst **2** gave only unsaturated material from reactions of **9a** (reaction 5) but significant amount of saturated products **14b** and **15b** were obtained from comparable reactions of **9b** (reaction 15). In contrast reactions using the phosphido-bridged W–Rh catalyst **1** gave significantly less saturated material from a reaction of **9b** than for a reaction of **9a** (cf. reactions 14 and 3). It is unlikely that these differences can be explained by the different reaction temperatures, 60°C for **9a** and 80°C for **9b**. Again preferential hydrogenation of the seven-ring intermediate was generally observed.

Reactions at 80°C but using higher pressures of H_2/CO were also carried out. Reactions using $[Rh(OAc)_2]_2/PPh_3$ under these conditions (reactions 7 and 8) surprisingly also gave significant amounts (> 30%) of unsaturated materials **12b**, **13b** and **17b** with only a small amount of hydrogenated material **14b** being observed (reaction 9). In addition, the 6-ring enamine **12b** was found in reactions using 1500 psi, 10.34 MPa of H_2/CO with $HRh(CO)(PPh_3)_3$ as catalyst (reactions 10 and 11). These reactions were carried out by different workers and in one case (reaction 10) gave some uncyclised linear aldehyde **11b** together with the aldehyde **16b** resulting from a second hydroformylation of the enamine **12b**. In contrast, reaction 11 under apparently identical conditions gave the saturated azepane **15b** as the major product.

*2.5. Reactions of N-benzyl-N-methylpent-4-enamide **19***



19 **20** **21**

Reactions of the amide **19** with H_2/CO using $[Rh(OAc)_2]_2/PPh_3$ and the bimetallic W–Rh catalysts **1** and **3** gave very similar ratios of the linear **20**- and branched **21**-aldehydes (about 60:40). Quantitative conversion was obtained at 60°C with the first two catalysts but only approx. 50% conversion was obtained using the cyclopentadienylphosphine compound **3**. Reactions using the bimetallic catalysts **1** and **3** at 40°C were very slow but the aldehydes obtained using **1** were still in the ratio 60:40 for **20**:**21**. Thus, these results show no evidence for chelation of the amido oxygen atom in the transition state which would lead to a preference for the branched product **21**. This result thus contrasts with reported reactions of pent-4-enamide itself using a range of rhodium catalysts at 100°C which gave only 5-methyl-2,3-dihydropyridin-2-one in excellent yields whose formation was rationalised in terms of amide-directed chelation control favouring initial formation of the branched aldehyde [24]. The influence of *N*-substitution on the regiochemistry of the initial hydroformylation reaction is possibly due to steric hindrance to chelation at the amido-oxygen. However, it has been previously shown that the regioselectivity of the initial hydroformylation of some mono-*N*-substituted but-3-enamides is not sensitive to the bulk of the substituent on nitrogen [24].

2.6. Conclusions

The variation in catalyst structure as a result of introducing bimetallic systems with phosphido bridges, i.e., catalysts **1**, **2** and **3** leads to very little change in the regioselectivity of hydroformylation of styrene, 1-hexene, some phosphinoalkenes and *N*-substituted pentenylamines and pentenylamides. The possibility that the heterobimetallic compounds were breaking down to monomeric rhodium species which then acted as catalysts was examined. Reactions using only a low substrate to catalyst ratio (4:1) allowed isolation of metallic species and the ^{31}P NMR spectrum of the product from a reaction of 1-hexene using **3** as catalyst showed retention of the W–Rh bond as W–Rh–P coupling was still observed. The regiochemistry of reactions of the phosphinoalkenes **4**; $n = 2$ or 3 was

dominated by chelation by phosphorus but reactions of the alkenylamines **9** showed no evidence for chelation by nitrogen. The results from the reactions with *N*-benzylpent-4-enylamine **9a** contrast with those reported previously where high regioselectivity for the product **14a** arising from *N*-chelation was obtained, e.g., using $HRh(CO)(PPh_3)_3$ as catalyst at 100°C with 1:1 H_2/CO (1800 psi, 12.40 MPa) [21]. In general, the reactions of the closely related amino substrates **9a** and **9b** showed considerable variation in chemoselectivity (see Tables 2 and 3) using the same catalyst although the reaction temperature was 20°C higher for reactions of **9b**. In view of the complex mixtures of products obtained from these reactions it appears that they are of very limited preparative value.

It appears that the regiochemistry of reaction is not influenced by the subtle differences in electronic distribution between the catalysts. In contrast, reactions of alkenylamines **9** were found to be very susceptible to steric effects associated with the use of the bulky bisphosphite ligand BIPHEPHOS [19,31,32].

3. Experimental

3.1. General methods

Most general methods were as described in a recent paper [33]. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solution. Gas chromatography (GLC) analysis was carried out using a 3700 Varian gas chromatograph using either a capillary 12QC5/BP5 column or a packed SE-30 column. Gas chromatography–mass spectroscopy (GCMS) was carried out using a Hewlett-Packard 5890 gas chromatograph with a BP5 column (25 m) coupled to a VG-TRIO-1 mass spectrometer (70 eV).

3.2. Preparation of substrates

The phosphinoalkenes **4**; $n = 1,2$ and 3 were prepared as described previously [10,22]. *N*-Phenylmethylpent-4-enylamine **9a** was prepared by $LiAlH_4$ reduction of the corresponding amide [21]. *N*-1-(Phenylethyl)pent-4-enylamine **9b** b.p. 100–105°C/0.1 mm [34] was prepared in a similar manner by $LiAlH_4$ reduction of *N*-(1-phenylethyl)pent-4-enamide.

3.3. Preparation of catalysts

Hydridocarbonyltris(triphenylphosphine)rhodium $HRh(CO)(PPh_3)_3$ was purchased from Aldrich. Rhodium acetate dimer, $[Rh(OAc)_2]_2$ was prepared as described by Legzdins et al. [35]. The phosphido bridged rhodium–tungsten compound $(OC)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ **1** was prepared as described by Shulman et al. [25].

*3.3.1. Tricarbonylmolybdenum(μ-η^5:η^1-cyclopentadienyldiphenylphosphine)dicarbonylrhodium, $(OC)_2Rh\text{-}Mo(CO)_3[\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PPh_2]$ **2***

Lithium (cyclopentadienyldiphenylphosphine)tricarbonylmolybdate, $Li[Mo(CO)_3(C_5H_4PPh_2)]$ was prepared by reaction of $(CH_3CN)_3Mo(CO)_3$ with lithium diphenylphosphinocyclopentadienide [36]. Reaction of this salt with μ-dichlorotetracarbonyldirhodium, $[Rh(CO)_2Cl]_2$ [37] was carried out under conditions described for the preparation of the corresponding bis-(*p*-tolyl)phosphine complex [26] and gave the title compound **2** as yellow-green crystals (49%) m.p., 173–175°C (decomp.). IR(CH_2Cl_2)

ν(CO): 2063 s, 1991 m, 1958 s, 1880 w, 1861 m cm^{-1}. ^1H NMR (400 MHz): δ(ppm) 4.41 (pseudoquartet, $J \approx 2$ Hz, 2 H, H3 and H4 of Cp), 5.50 (pseudoquartet, $J \approx 2$ Hz, 2 H, H2 and H5 of Cp), 7.52 (m, 6 H, *m*- and *p*-H of C_6H_5), 7.94 (m, 4 H, *o*-H of C_6H_5). ^{31}P NMR (162 MHz): δ (ppm) + 44.3 (d, J_{Rh-P} 116 Hz). ^{13}C NMR (50 MHz, $CDCl_3$ + $Cr(acac)_3$): δ (ppm) 58.4 (d, J_{P-C} 53.5 Hz, C1 of Cp), 92.2 (m, Cp), 120.0 (d, J_{P-C} 49.2 Hz, ArC), 129.3 (d, J_{P-C} 11.1 Hz, *m*-ArCH), 132.2 (d, J_{P-C} 2.4 Hz, *p*-ArCH), 134.0 (d, J_{P-C} 14.1 Hz, *o*-ArCH), 221.6 (s, $Mo(CO)_2$), 233.4 (s, Mo(CO)). Elemental analysis (%), found: C, 44.7; H, 2.5; P, 5.0. $C_{22}H_{14}MoO_5PRh$ requires C, 44.9; H, 2.4; P, 5.3.

3.3.2. *Tricarbonyltungsten(μ-η⁵:η¹-cyclopentadienyldiphenylphosphine)dicarbonylrhodium, $(OC)_2$Rh-W(CO)$_3$[μ-η⁵:η¹-$C_5H_4PPh_2$]* **3**

The W–Rh analogue **3** was prepared in a similar manner to that described above [26,36]. $(CH_3CN)_3W(CO)_3$ was prepared by reaction of $W(CO)_6$ and CH_3CN under reflux for 120 h and reaction with lithium diphenylphosphinocyclopentadienide gave a THF solvate of Li[$W(CO)_3$-($C_5H_4PPh_2$)]. Reaction of this salt with $[Rh(CO)_2Cl]_2$ gave the title compound **3** as olive green crystals (41%) m.p. 162-165°C (decomp). IR (Nujol) ν(CO): 2060 s, 1986 s, 1942 s (br), 1864 s, 1855 s, 1842 s cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ (ppm) 3.87 (pseudoquartet, J 2 Hz, 2 H, H3 and H4 of Cp), 4.64 (pseudoquartet, J 2 Hz, 2 H, H2 and H5 of Cp, 6.90–7.01 (m, 6 H, *m*- and *p*-H of C_6H_5), 7.69 (dd, J_{P-H} 12.5, J_{H-H} 8.0 Hz, *o*-H of C_6H_5). ^{13}C NMR (C_6D_6, 100 MHz): δ (ppm) 59.6 (d, J_{P-C} 52.5 Hz, C1 of Cp), 89.7 (s, C3 of Cp), 89.7 (d, J_{P-C} 5.6 Hz, C2 of Cp), 129.3 (d, J_{P-C} 11.2 Hz, *m*-ArCH), 129.4 (d, J_{P-C} 48.3 Hz, ArC), 132.0 (d, J_{P-C} 2.5 Hz, *p*-ArCH), 134.1 (d, J_{P-C} 14.1 Hz, *o*-ArCH), 184.3 (bs, Rh(CO), *trans* to P), 200.2 (dd, J_{Rh-C} 64.4 Hz, J_{P-C} 113.7 Hz, Rh(CO), *trans* to W), 210.3 (s, with ^{183}W satellites, J_{W-C} 169 Hz, $W(CO)_2$), 223.1 (s with ^{183}W satellites, J_{W-C} 165 Hz, W(CO)). ^{31}P NMR (C_6D_6, 121.5 MHz): δ (ppm) 41.0 (d, J_{Rh-P} 122.5 Hz, with ^{183}W satellites, J_{W-P} 21.5 Hz). Elemental analysis (%), found: C, 39.2; H, 2.0. $C_{22}H_{14}WO_5Rh$ requires C. 39.1; H, 2.1.

3.4. Hydroformylation reactions

3.4.1. General conditions

Reactions were carried out using H_2/CO (1:1) in the initial pressure range 400–1500 psi (2.76–10.34 MPa) in a Parr 100 ml stainless steel autoclave with a glass liner. The temperature was measured using a thermocouple inserted between the autoclave and the heating block. All reactions were carried out at temperatures in the range 40–80°C in magnetically stirred ethyl acetate or benzene solutions. The substrate:Rh ratio was about 100:1. The reactions were allowed to cool and the solvent removed under vacuum. When air-sensitive samples were hydroformylated, the samples were transferred to a Schlenk flask under an atmosphere of nitrogen. The solvent was then evaporated under vacuum. Isomer ratios were determined from the ^1H NMR spectra of the crude reaction mixture. GLC was also used for determining the isomer ratios.

3.4.2. Reactions of styrene and 1-hexene

In a typical reaction, $(OC)_2RhMo(CO)_3(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PPh_2)$ **2** (16.6 mg, 0.0282 mmol) and styrene (0.29 g, 0.28 mmol) (ratio 1:100) in benzene (15 ml) were reacted with hydrogen and carbon monoxide (400 psi, 2.76 MPa) according to the general procedure for 22 h at 50°C. Evaporation of the solvent gave the crude product as a dark oil (0.36 g, 97%). A ^1H NMR spectrum indicated that no

starting material was present and that the crude product consisted of a mixture of the two aldehyde isomers 2-phenylpropanal and 3-phenylpropanal in the ratio 95:5.

Reactions of 1-hexene were carried out under identical conditions using $[Rh(OAc)_2]/PPh_3$ and the cyclopentadienylphosphine **3**. The product ratio was based on integration of the C**H**O absorptions at δ 9.76 (t, J 1.9 Hz) for heptanal and at δ 9.61 (d, J 2.1 Hz) for 2-methylhexanal in the ^{1}H NMR spectrum of the total product.

A reaction was carried out using 1-hexene (13.6 mg, 0.16 mmol) and the cyclopentadienyphosphine **3** (27.4 mg, 0.04 mmol) in benzene (10 ml) with H_2/CO, (400 psi, 2.76 MPa) at 60°C for 20 h. The solvent and product aldehydes were distilled off under reduced pressure (0.1 mm) at 20°C and the residue, a yellow-brown solid examined spectroscopically. IR (C_6D_6) ν_{CO} 2062 s, 1987 s, 1956 s (br), 1881 s and 1861 s cm^{-1}. ^{1}H and ^{31}P NMR spectra were identical to those reported above for **3**.

*3.4.3. Reactions of the phosphinoalkenes **4**; n = 1, 2, and 3*

Hydroformylation of the phosphinoalkenes **4** was carried out using the appropriate catalyst at 80°C for 20 h and the resulting products analysed by ^{1}H and ^{31}P NMR spectroscopy. Product identification was by comparison with published data [22].

*3.4.4. Reactions of aminoalkenes **9a** and **9b***

Reactions of *N*-phenylmethylpent-4-enamine **9a** were carried out as described above under a range of conditions as summarised in Table 2. The product ratios were determined using ^{1}H NMR spectroscopy by integration of the olefinic protons in compounds **12**, **13**, and **17**, the benzyl CH_2 of **12**, **14** and **15** and the CH_3 doublet of **14**. The spectra were assigned on the following basis: A sample of 5-methyl-1-phenylmethyl-1,2,3,4-tetrahydropyridine **12a** was isolated from the products of reaction 1 (Table 2) as an oil, ^{1}H NMR (400 MHz): δ (ppm) 1.59 (s, 3 H, CH_3), 1.93 (m, 4 H, H3, H4), 2.70 (m, 2 H, H2), 3.80 (s, 2 H, CH_2Ph), 5.71 (bs, 1 H, H6), 7.23 (m, 5 H, Ph). ^{13}C NMR (100 MHz): δ (ppm) 21.25, (CH_3), 22.9, 27.2 (C3, C4), 54.2 (C2), 60.2 (CH$_2$Ph), 106.9 (C5), 127.2, 128.3, 128.45 (ArCH), 131.7 (C6), 139.0 (C1′). MS(ESI): m/z 188.1 $(M+H)^+$. HRMS (ESI) m/z found: 188.1440. Calc. for $(C_{13}H_{18}N)^+$ 188.1439. The spectral data were in agreement with literature values [38].

1-Phenylmethyl-3-methylpiperidine **14a** had ^{1}H NMR (400 MHz): δ (ppm) 0.83 (d, J 6.0 Hz, 3 H, CH_3), 1.68 (m, 5 H, H3, H4, H5), 2.74 (m, 4 H, H2, H6), 3.43 (s, 2 H, CH_2Ph), 7.23 (m, 5 H, Ph). ^{13}C NMR (100 MHz): δ (ppm) 20.0 (CH_3), 25.6 (C4 or C5), 31.3 (C3), 33.3 (C4 or C5), 54.2, 62.15, 63.8 (C2, C6, CH$_2$Ph), 126.9, 128.1, 128.3 (ArCH). MS (ESI): m/z 189.9 $(M+H)^+$. HRMS (ESI) m/z found: 190.1595. Calc. for $(C_{13}H_{20}N)^+$: 190.1595. Data were in agreement with literature values [21].

A sample of 1-(phenylmethyl)azepane **15a** prepared by benzylation of hexamethylenimine (**15**; R = H) had ^{1}H NMR (400 MHz): δ (ppm) 1.62 (bs, 8 H, H3, H4, H5, H6), 2.69 (t, J 5.3 Hz, 4 H, H2, H7), 3.60 (s, 2 H, CH_2Ph), 7.23 (m, 5 H, Ph). ^{13}C NMR (100 MHz): δ (ppm) 26.6, 27.8 (C3, C4, C5, C6), 55.2 (C2, C7), 62.3 (CH$_2$Ph), 126.3, 127.7, 128.4 (ArCH), 139.7 (ArC). MS(ESI): m/z 189.9 $(M+H)^+$. HRMS (ESI) m/z found: 190.1595. Calc. for $(C_{13}H_{20}N)^+$ 190.1595. Data were in agreement with literature values [21].

1-(Phenylmethyl)-1,2,3,4,5-tetrahydro-1*H*-azepine **13a** not isolated as a pure compound had ^{1}H NMR (400 MHz): δ (ppm) 5.18 (dt, J 15.3, 7.2 Hz, 1 H, H6), 5.93 (d, J 15.3 Hz, 1 H, H7). ^{13}C NMR (100 MHz): δ (ppm) 119.45 (C6), 134.45 (C7). GCMS: m/z 187(M^+, 26%), 186 (30), 172 (17), 96 (22), 91 (100), 68(50). HRMS (ESI) m/z found: 188.1440. Calc. for $(C_{13}H_{18}N)^+$:

188.1439. Structure proof came from hydrogenation of the product from reaction 2 (Table 2) using $[Rh(OAc)_2]_2$ (3.0 mg), BIPHEPHOS (10.0 mg) and H_2 (400 psi) at 80°C for 20 h. The product was shown to be a mixture of the azepane **15a** together with the saturated dimer **18a**.

6-(1-phenylmethylazepan-2-yl)-1-phenylmethyl-2,3,4,5-tetrahydro-1*H*-azepine **17a** had ^{1}H NMR (400 MHz): δ (ppm) 6.04 (bs, 1 H, H7). ^{13}C NMR (100 MHz): δ (ppm) 114.0 (C6), 141.8 (C7). MS (EI): m/z 376 (M^+, 4%), 285 (12), 200 (38), 91 (100).

Hydrogenation of the product from reaction 2 as described above gave the saturated dimer **18a**.

Similar reactions of *N*-(1-phenylethyl)pent-4-enamine **9b** are summarised in Table 3. The product ratios were again established on the basis of ^{1}H NMR spectra using the olefinic protons of **12b**, **13b** and **17b** and the C*H*Ph quartets. Spectral assignments were made on the following basis: 5-methyl-1-(1-phenylethyl)-1,2,3,4-tetrahydropyridine **12b** was isolated by chromatography of the product from reaction 7 (Table 3) on neutral alumina. ^{1}H NMR (300 MHz): δ (ppm) 1.44 (d, J 6.9 Hz, 3 H, CH_3CH), 1.59 (bs, 3 H, CH_3–C5), 1.76–1.88 (m, 4 H, H3, H4), 2.71 (m, 2 H, H2), 3.99 (q, J 6.9 Hz, 1 H, C*H*CH_3), 5.86 (bs, 1 H, H6), 7.22–7.32 (m, 5 H, Ph). ^{13}C NMR (50 MHz): δ (ppm) 18.0 (*C*H_3CH), 21.2 (*C*H_3–C5), 22.8, 27.0 (C3, C4), 44.6 (C2), 61.5 (*C*HCH_3), 126.7, 127.2, 128.1 (ArCH), 128.9 (C6), 143.4 (ArC). MS(ESI): m/z 202.2 $(M+H)^+$. MS (EI): m/z 201 (M^+, 42%), 186 (9), 174 (14), 105 (100), 97 (11), 91 (7), 77 (12), 56 (18). HRMS (ESI) m/z found: 202.1586. Calc. for $(C_{14}H_{20}N)^+$: 202.1596. HRMS (EI) m/z found: 201.152 ± 0.002. Calc. for $(C_{14}H_{19}N$: 201.152.

3-Methyl-1-(1-phenylethyl)piperidine **14b** had ^{1}H NMR (200 MHz): δ (ppm) 0.9 (d, J 7 Hz, 3 H, CH_3).

1-(1-Phenylethyl)azepane **15b**. A sample of this compound was isolated by chromatography of the product from reaction of **9b** with H_2/CO, 9:1 in the $[Rh(OAc)_2]_2$/BIPHEPHOS at 80° for 20 h as an oil, b.p. 130° (oven)/0.4 mm. An authentic sample (90%) was prepared by alkylation of hexamethyleneimine with 1-bromoethylbenzene. ^{1}H NMR (300 MHz): δ (ppm) 1.35 (d, J 6.8 Hz, 3 H, CH_3), 1.57 (bs, 8 H, H3, H4, H5, H6), 2.62 (bs, 4 H, H2, H7), 3.76 (q, J 6.7 Hz, 1 H, *CH*CH_3), 7.18–7.44 (m, 5 H, Ph). ^{13}C NMR (50 MHz): δ (ppm) 18.2 (CH_3), 27.0, 28.85 (C3, C4, C5, C6), 52.0 (C2, C7), 63.15 (*C*HCH_3), 126.4, 127.5, 127.9 (ArCH), 144.8 (ArC). MS (ESI): m/z 204.0 $(M+H)^+$. MS(EI): m/z 203 (M^+, 9%). 189 (13), 188 (100), 126 (35), 105 (56), 77 (20) HRMS (ESI) m/z found: 204.1746. Calc. for $(C_{14}H_{22}N)^+$: 204.1752.

1-(1-Phenylethyl)-2,3,4,5-tetrahydro-1*H*-azepine **13b** had ^1H NMR (300 MHz): δ (ppm) 5.15 (dt, J 15.3, 6.9 Hz, 1 H, H6), 5.94 (d, J 15.3 Hz, 1 H, H7) ^{13}C (50 MHz): δ (ppm) 118.6 (C6), 134.2 (C7). GCMS m/z: 201 (M^+, 40%), 186 (47), 124 (10), 105 (100), 97 (40), 96 (23), 82 (90), 79 (40), 77 (42). HRMS (ESI) m/z found: 202.1583. Calc. for $(C_{14}H_{20}N)^+$: 202.1596. Hydrogenation, as described above, of the product from reaction 12, rich in this material, gave the azepane **15b**.

6-[1-(1-Phenylethyl)azepan-2-yl]-1-(1-phenylethyl)-2,3,4,5-tetrahydro-1*H*-azepine **17b** had ^{1}H NMR (300 MHz): δ (ppm) 6.18 (bs, 1 H, H7). ^{13}C (50 MHz): δ (ppm) 139.9 (C7). Hydrogenation of the product from reaction 12 followed by chromatography (silica, 50% ethyl acetate/light petroleum) gave a sample of 1,1′-di(1-phenylethyl)-2,3′-bis(azepane) **18b**. (Mixture of isomers) — ^{1}H NMR (400 MHz): δ (ppm) 1.04–1.24 (m, 16 H), 1.32–1.36 (m, 12 H, CH_3CHPh), 1.37–1.70 (m, 16 H), 2.15–2.25 (m, 2 H, CH_2N) 2.35–2.51 (m, 5 H, CH_2N), 2.54–2.73 (m, 5 H, CH_2N), 3.69–3.85 (m, 4 H, C*H*Ph), 7.16–7.39 (m, 20 H, ArH). ^{13}C NMR (100 MHz): δ (ppm) 16.5, 18.4, 24.35 (*C*H_3CH), 25.18, 25.23 27.32, 27.36, 29.6, 29.8, 29.85, 30.3, 33.7, 33.9, 35.32, 35.35 (CH_2), 39.3, 39.8 (CH), 47.9, 52.6, 52.7, 57.6 (CH_2N), 58.4, 63.4, 64.0 (*C*HCH_3), 126.43, 126.44, 126.6, 126.8, 127.65, 127.7, 127.88, 127.93, 128.4 (ArCH), 144.8, 145.2, 146.0 (ArC). MS (ESI): m/z 405.3 $(M+H)^+$, 443.3 $(M+K)^+$. HRMS (ESI) m/z found: 405.3265. Calc. for $(C_{28}H_{41}N_2)^+$: 405.3270. An identical

sample was obtained from the reaction of **9b** with H_2/CO, 9:1 using $[Rh(OAc)_2]_2$/BIPHEPHOS after removal of the azepane **15b** by distillation as described above.

*3.4.5. Reactions of the amidoalkene **19***

Reactions of *N*-methyl-*N*-phenylmethylpent-4-enamide **19** were carried out as described above using the appropriate catalyst at 40 or 60°C for 20 h and the products analysed by ^1H and ^{13}C NMR spectroscopy. The product was a mixture of the two aldehyde isomers *N*-methyl-*N*-phenylmethyl-6-oxohexanamide **20** and *N*-methyl-*N*-phenylmethyl-4-methyl-5-oxopentanamide **21** in the ratio 60:40 and spectral data are reported on this mixture. ^1H NMR (300 MHz) [1]: δ (ppm) 1.06 (d, J 7.1 Hz, CCH_3, **21b**), 1.13 (d, J 7.1 Hz, CCH_3, **21a**), 1.65–1.83 (m, H3 and H4, **20**; H3, **21**), 2.07 (m, H4, **21**), 2.35–2.46 (m, H2 and H5, **20**; H2, **21**), 2.89 (s) and 2.92 (s) (CH_2Ph), 4.52 (s) and 4.57 (s) (NCH_3), 7.12–7.34 (m, Ph), 9.56 (d, J 1.7 Hz, H5, **21b**), 9.62 (d, J 1.8 Hz, H5, **21a**), 9.69 (t, J 1.6 Hz, H6, **20b**), 9.73 (t, J 1.6 Hz, H6, **20a**). ^{13}C NMR (100 MHz) [1]: δ (ppm) 13.5 (CCH_3, **21b**), 13.6 (CCH_3, **21a**), 21.8, 24.6, 24.8, 25.7, 25.9, 30.1, 32.7, 33.1 (C3, C4 and C5, **20**; C3, **21**), 34.0, 34.1, 34.8 (NCH_3), 43.7, 43.75 (C2, **20**; C2, **21**), 45.7, 45.8 (C4, **21**), 50.8, 50.84, 53.3 (CH_2Ph), 126.3, 127.3, 127.6, 128.0, 128.4, 128.6, 129.0 (ArCH), 136.8, 137.4, 137.5 (ArC), 172.2, 172.6, 172.9 (C1, **20**; C1, **21**), 202.4, 204.6, 204.7 (C6, **20**; C5, **21**). GCMS for **20**: m/z 233 (M^+, 7%), 205(10), 190(15), 176(22), 163(35), 162(13), 120(56), 106(28), 91(100), 65(21). GCMS for **21**: m/z 233 (M^+, 10%), 204(9), 176(20), 163(55), 162(19), 120(52), 106(20), 91(100), 65(20), 55(25). HRMS (ESI) m/z found: 234.1483. Calc. for $(C_{14}H_{20}NO_2)^+$: 234.1494.

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