Hydroformylation of alkenes and alkynes using a heterobinuclear Rh–W catalyst

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Abstract

Hydroformylation reactions of a series of alkenes and alkynes have been carried out using the heteronuclear Rh–W catalyst, $(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ (**1**). The results of these reactions have been compared with corresponding reactions using $[Rh(OAc)_2]_2$ as catalyst. Catalysis of a reaction of styrene using **1** gave a very high yield of the branched chain aldehyde containing only a trace of the straight chain isomer. Reactions of the phosphinoalkene, $Ph_2P(CH_2)_3CH{=}CH_2$ (**7**) and the corresponding alkyne, $Ph_2P(CH_2)_3C{\equiv}CH$ (**11**) gave similar products using either catalyst system with the alkyne reaction being significantly slower. Reaction of the alkenyl dithiane, $S(CH_2)_3SCH{-}CH_2CH{=}CH_2$ (**2**), using the Rh–W catalyst (**1**) gave a higher ratio of linear to branched aldehydes (47 linear:53 branched) than the corresponding reaction using $[Rh(OAc)_2]_2$ (25 linear:75 branched). Reactions of vinyl acetate using **1** as catalyst gave a significant amount of linear aldehyde in contrast to reactions using $[Rh(OAc)_2]_2$ but reactions of allyl acetate gave similar products for both catalyst systems.

Key words: Hydroformylation; Alkenes; Alkynes; Rhodium complexes; Tungsten complexes; Heterobinuclear complexes

Introduction

There is much current interest in the use of both homo- and heterobinuclear metal complexes as catalysts in hydroformylation reactions [1, 2]. Enhancement of both reactivity and selectivity have been claimed. In this paper we explore the use of a heterobinuclear Rh–W compound $(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ (**1**) [3] as a catalyst for the hydroformylation of a range of alkenes and alkynes. The effect of remotely substituted phosphorus and sulfur substituents on the regioselectivity of these reactions has been compared with reactions carried out with $[Rh(OAc)_2]_2$ as a catalyst in order to evaluate the preferential site of coordination. Reactions of some typical alkenes – styrene, vinyl acetate and allyl acetate – have also been carried out using the Rh–W catalyst to provide points of reference.

Experimental

General procedures

All reactions involving phosphines and rhodium catalysts were carried out under an atmosphere of nitrogen in oven dried Schlenk flasks where appropriate. Purification was achieved by column chromatography on neutral alumina (Merck, aluminium oxide) or by Kugelrohr distillation (temperatures reported are oven temperatures and serve only as a guide). Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Hydroformylation reactions

Hydroformylation reactions were carried out in a 100 ml stainless steel Parr autoclave equipped with a glass sleeve and magnetic stirrer. The autoclave and solvent were flushed thoroughly with nitrogen before the addition of the substrate and catalyst. The autoclave was then flushed several times with a 1:1 molar mixture of carbon monoxide and hydrogen (3 × 200 psi), pressurised to the required pressure and heated to reaction temperature. Regulation of the reaction temperature was achieved by use of a thermocouple inserted between the autoclave and heating block. After reaction the autoclave was cooled and the contents transferred to another flask, under nitrogen for air-sensitive products.

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Isomer ratios were determined immediately after reaction from ^{1}H NMR spectral data.

Instrumentation

IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. NMR spectra were measured on Bruker AC200 or AM300 spectrometers. The ^{1}H NMR spectra were measured at 200 or 300 MHz, ^{13}C at 50 MHz and ^{31}P at 121.5 MHz; deuterated solvent ($CDCl_3$) was used as internal lock. Chemical shifts are in parts per million from internal Me_3Si for ^{1}H and ^{13}C, and from external 85% H_3PO_4 for ^{31}P; in all cases, a positive chemical shift denotes a shift downfield from the reference. Electron impact mass spectra were obtained by using a VG micromass 70/70-F or VG Trio-1 spectrometer operating at 70 eV and 200 °C inlet temperature. Accurate mass determinations were made at high resolution on the VG micromass 70/70-F instrument by peak matching with an internal standard. Ultrasonic reactions were carried out using a conventional cleaning bath (Ultrasonics Pty Ltd., Sydney, Australia). Preparative radial chromatography was carried out using a Chromatotron model 7924T on glass plates coated with alumina.

Materials

Solvents were of analytical grade and purified by standard procedures [4]. 'X4' refers to a petroleum fraction of boiling point 30–60 °C. All solvents were purged with nitrogen prior to use. $[Rh(OAc)_2]_2$ was prepared as described by Wilkinson and co-workers [5]. $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) was prepared as described by Geoffroy and co-workers [3]. 3-(1,3-Dithian-2-yl)prop-1-ene (**2**) was prepared by E. Tasdelen following the method of Seebach and Corey [6].

Preparation of phosphinoalkenes and -alkynes [7]

$Ph_2P(CH_2)_2CH{=}CH_2$ (5)

In a typical procedure following the method of Chou *et al.* [7] a mixture of PPh_3 (2.40 g, 9.15 mmol) and freshly chopped Li (0.64 g, 92 mmol) in tetrahydrofuran (50 cm^3) was irradiated in an ultrasonic bath for 2 h 45 min. The color of the reaction mixture changed from clear to deep red. The solution was removed from unchanged Li via cannula and t-butyl chloride (0.776 g, 8.4 mmol) in tetrahydrofuran (4 cm^3) was added slowly. The reaction mixture was cooled to 0 °C and $Br(CH_2)_2CH{=}CH_2$ (1.1 g, 8.2 mmol) was added dropwise. After addition was complete the solution was a pale red colour. The solution was refluxed for 1 h then stirred overnight at room temperature. Solvent removal gave a white oily solid which was taken up in toluene (25 cm^3) and washed with water (3×10 cm^3). The organic layer was dried (Na_2CO_3), filtered and the solvent removed under reduced pressure to give a light yellow oil which was purified using column chromatography (alumina, neutral Act I, X4/toluene 3:1) to give the title compound **5** as a clear oil (0.59 g, 30%). The spectral data (IR, ^{1}H NMR, ^{31}P NMR and MS) were identical to those reported in the literature [8, 9].

$Ph_2P(CH_2)_3CH{=}CH_2$ (7)

In a similar manner, a solution of $Br(CH_2)_3CH{=}CH_2$ (1.26 g, 8.45 mmol) in tetrahydrofuran (8 cm^3) was added to a freshly prepared solution of $LiPPh_2$ (prepared from PPh_3 (2.40 g, 9.15 mmol) and Li (0.64 g, 92 mmol)). Workup as above gave a crude oil which was purified by Kugelrohr distillation to give the title compound **7** as a colourless oil (0.50 g, 21%) b.p. (oven) 175 °C/0.03 mm. Lit. [9]: 118–128 °C/0.2 mm. Spectroscopic data: ^{31}P NMR ($CDCl_3$) δ −15.66 (s). IR, ^{1}H NMR and MS data were identical to those reported in the literature [8, 9].

$Ph_2P(CH_2)_3C{\equiv}CH$ (11)

A mixture of Li (0.54 g, 78 mmol) and PPh_3 (2.40 g, 9.15 mmol) in tetrahydrofuran (40 cm^3) was irradiated in an ultrasonic bath for 24 h. The deep red solution was removed from unchanged Li via cannula, ^{t}BuCl (0.85 g, 9.20 mmol) was added, and the resultant solution was added dropwise over a period of 20 min to $Cl(CH_2)_3C{\equiv}CH$ (0.94 g, 9.2 mmol) at 0 °C. Stirring was continued for 17 h at ambient temperature. Workup as described above gave the crude product as a yellow oil which was purified by Kugelrohr distillation to give the title compound **11** as a clear oil (0.82 g, 36%) b.p. (oven) 140 °C/0.035 mm. Accurate mass MS: calc. for $C_{17}H_{17}P$: 252.107; found 252.106 ± 0.002. Spectroscopic data: IR (film): ν3298(s), 3071(m), 2929(s), 2862(m), 2117(w), 1586(w), 1481(m), 1434(s), 739(s), 696(vs), 632(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.67 (m, 2H, H4); 1.96 (t, 1H, $J_{H3,H1}$ = 2.6 Hz, H1); 2.17 (m, 2H, H5); 2.30 (td, 2H, $J_{H4,H3}$ = 6.9, $J_{H1,H3}$ = 2.6 Hz, H3); 7.2–7.6 (m, 10H, 2Ph). ^{31}P NMR ($CDCl_3$): δ −16.47(s). MS, *m/z* (relative intensity): 252 (75%, M^+), 251 (100, $C_{17}H_{16}P^+$), 237 (31), 224 (78), 199 (25), 185 (54, $C_{12}H_{10}P^+$), 183 (81, $C_{12}H_8P^+$), 133 (20), 108 (32, $C_5H_5P^+$), 107 (31), 91 (58), 77 (14), 51 (14).

Hydroformylation reactions of alkenes and alkynes with $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$

Styrene

In a typical reaction $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (40.8 mg, 0.0309 mmol) and styrene (0.38 g, 3.6 mmol) (ratio 1:100) in benzene (15 cm^3) were reacted with hydrogen and carbon monoxide (380 psi) according to the general procedure for 22 h at 50 °C. The solvent was removed to give a dark brown oil (0.48

g, 98%) which was shown by spectroscopic data to consist of a mixture of 2-phenylpropanal and 3-phenylpropanal in the ratio 94:6 respectively. No starting material was evident. The ^{1}H NMR data for the two aldehydes were consistent with values obtained for authentic samples.

Another reaction carried out under similar conditions but for 20 h and with a catalyst to substrate ratio of 1:80 gave 2-phenylpropanal and 3-phenylpropanal in quantitative yield in the ratio 98:2, respectively.

Vinyl acetate

Reaction of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (17.8 mg, 0.0135 mmol) and vinyl acetate (0.135 g, 1.57 mol) (ratio 1:100) in benzene (15 cm^3) with H_2/CO (380 psi) for 22 h at 50 °C gave an orange oil (0.13 g, 72%) which was shown by ^{1}H NMR spectroscopy to be a mixture of 2-acetoxypropanal and 3-acetoxypropanal in the ratio 75:25. No starting material was evident. The ^{1}H NMR spectral data were identical with literature values [10].

Allyl acetate

Reaction of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (42.8 mg, 0.0324 mmol) and allyl acetate (0.38 g, 3.8 mmol) (ratio 1:100) in benzene (15 cm^3) with H_2/CO (380 psi) for 22 h at 50 °C gave a yellow oil (0.44 g). The ^{1}H NMR spectrum of the oil showed a mixture of 3-acetoxy-2-methylpropanal and 4-acetoxybutanal in the ratio 11:89. There was a significant amount of two other aldehydes which were not identified.

3-(1,3-Dithian-2-yl)prop-1-ene (2)

$(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (16.1 mg, 0.0122 mmol) and 3-(1,3-dithian-2-yl)prop-1-ene (**2**) (0.23 g, 1.43 mmol) (ratio 1:100) in benzene (15 cm^3) were reacted with H_2/CO (380 psi) for 20 h at 50 °C to give a yellow oil (0.19 g). Comparison of the ^{1}H NMR data with reported values [11] indicated a mixture of starting material (8%) and the two aldehydes 3-(1,3-dithian-2-yl)-2-methylpropan-1-al (**3**) and 4-(1,3-dithian-2-yl)butan-1-al (**4**) in the ratio 53:47 (92%) (combined yield of aldehydes *c.* 76%). The IR and ^{1}H NMR data were identical to those reported [11].

$Ph_2P(CH_2)_2CH{=}CH_2$ (5)

$Ph_2P(CH_2)_2CH{=}CH_2$ (**5**) (0.86 g, 3.6 mmol) and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (40.2 mg, 0.0304 mmol) (ratio 100:1) in benzene (15 cm^3) were reacted with H_2/CO (380 psi) at 80 °C for 22 h. Solvent removal gave a yellow oil (0.75 g, 77%) which was shown by ^{31}P and ^{1}H NMR data to consist solely of 4-diphenylphosphino-2-methylbutan-1-ol (**6**). IR, ^{1}H NMR and ^{31}P NMR data were identical with those reported in the literature [8].

$Ph_2P(CH_2)_3CH{=}CH_2$ (7)

Reaction of $Ph_2P(CH_2)_3CH{=}CH_2$ (**7**) (0.36 g, 1.4 mmol) and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (16.4 mg, 0.012 mmol) (ratio 100:1) in benzene (15 cm^3) with H_2/CO (380 psi) at 80 °C for 22 h gave the crude product as a yellow oil (0.43 g, 100%). The ^{1}H NMR spectral data showed a mixture of 5-diphenylphosphino-2-methylpentan-1-al (**8**), 5-diphenylphosphino-2-methylpentan-1-ol (**10**) and 5-diphenylphosphinohexan-1-al (**9**) in the ratio of 77:12:6. The IR and ^{1}H NMR spectral data were identical with those reported in the literature [8].

$Ph_2P(CH_2)_3C{\equiv}CH$ (11)

Reaction of $Ph_2P(CH_2)_3C{\equiv}CH$ (**11**) (0.33 g, 1.3 mmol) and $(CO)_4\overline{W(\mu\text{-}PPh_2)_2}RhH(CO)(PPh_3)$ (**1**) (15.2 mg, 0.0150 mmol) (ratio 100:1) in benzene (15 cm^3) with H_2/CO (380 psi) at 80 °C for 22 h gave a yellow oil (0.36 g). The ^{1}H NMR spectrum of the crude product showed the starting alkyne **11** (61%) and 5-diphenylphosphino-2-methylpentan-1-al (**8**) (39%) (quantitative recovery). IR, ^{1}H NMR and ^{31}P NMR spectral data for **8** were identical to those obtained for **8** from the reaction of the phosphinoalkene **7** above.

Hydroformylation reactions of $Ph_2P(CH_2)_3CH{=}CH_2$ (7) and $Ph_2P(CH_2)_3C{\equiv}CH$ using $[Rh(OAc)_2]_2$ (11)

$Ph_2P(CH_2)_3C{\equiv}CH$ (11)

$[Rh(OAc)_2]_2$ (4.5 mg, 0.010 mmol) and $Ph_2P(CH_2)_3C{\equiv}CH$ (**11**) (0.52 g, 2.1 mmol) (ratio 1:200) in benzene (15 cm^3) were reacted with H_2/CO (500 psi) for 22 h at 100 °C. Workup gave an orange oil (0.49 g) whose ^{1}H NMR and ^{31}P NMR spectra showed the starting alkyne (45%) and 5-diphenylphosphino-2-methylpentan-1-al (**8**) (55%).

A further reaction using $Ph_2P(CH_2)_3C{\equiv}CH$ (**11**) (0.58 g, 2.3 mmol) under the same conditions for 48 h gave an orange oil (0.57 g, 87%). The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of the crude product indicated complete reaction of the substrate to give a mixture of 5-diphenylphosphino-2-methylpentan-1-al (**8**) and 5-diphenylphosphino-2-methylpentan-1-ol (**10**) in the ratio 75:25. IR, ^{1}H NMR and ^{31}P NMR spectral data were identical to that reported in the literature [8].

The mixture of aldehyde **8** and alcohol **10** was completely characterised as the corresponding phosphorylcarboxylic acid derivative following the method described by Masamune and co-workers [12]. A solution of the crude hydroformylation product (0.57 g) in t-BuOH (20 cm^3) was treated with an aqueous solution of NaH_2PO_4 (5%, 35 cm^3) to give a solution of pH 5. An aqueous $KMnO_4$ solution (1.0 M, 25 cm^3) was added with vigorous stirring at room temperature. Stirring was continued for 10 min and the reaction was quenched by the addition of a saturated solution of Na_2SO_3 (30

cm^3) resulting in the precipitation of MnO_2. This was dissolved by the addition of cool (0 °C) dilute HCl to pH 3. This solution was extracted with dichloromethane (4×50 cm^3), the extract was dried ($MgSO_4$), and the solvent removed under reduced pressure to give a clear pale yellow oil which crystallised upon standing to give 5-diphenylphosphoryl-2-methylpentanoic acid (**12**) as an off-white crystalline solid (0.40 g, 69%). (Yield based on starting alkyne, 61%). M.p. 119–120 °C. *Anal.* Calc. for $C_{18}H_{21}O_3P$: C, 68.3; H, 6.7; P 9.8. Found: C, 68.0; H 6.9; P 9.5%. Spectroscopic data: IR (film): ν 3057(m), 1716(vs), 1592(w), 1485(w), 1463(m), 1438(s), 1266(m), 1216(m), 1152(vs), 1122(s), 1100(m), 734(vs), 676(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.09 (d, 3H, $J_{CH_3,H2} = 6.9$ Hz, CH_3); 1.41–1.86 (m, 4H, H3, H4); 2.26–2.47 (m, 3H, H2, H5); 7.45 (m, 6H) and 7.73 (m, 4H) (2Ph); 9.97 (br s, 1H, H1). ^{13}C NMR ($CDCl_3$): δ 17.10 (CH_3), 19.25 (d, $^2J_{PC} = 3.4$ Hz, C4), 29.09 (d, $^1J_{PC} = 71.8$ Hz, C5); 34.73 (d, $^3J_{PC} = 15.1$ Hz, C3); 38.97 (C2); 128.58, 128.82, 130.63, 130.66, 130.82, 130.85, 131.89, 131.94, 132.77, 132.81 (2 Ph); 179.0 (C1). ^{31}P NMR ($CDCl_3$): $\delta + 35.61$ (s). MS, *m/z* (relative intensity): 316 (16% M^+), 271 (23, $C_{17}H_{20}OP^+$), 229 (20, $C_{14}H_{13}OP^+$), 216 (100, $C_{13}H_{13}OP^+$), 215 (92, $C_{13}H_{12}OP^+$), 202 (92, $C_{12}H_{11}OP^+$), 201 (92, $C_{12}H_{10}OP^+$), 183 (10, $C_{12}H_8P^+$) 155 (10), 125 (19), 77 (36), 51 (11).

$Ph_2P(CH_2)_3CH{=}CH_2$ (7)

Reaction of $[Rh(OAc)_2]_2$ (4.8 mg, 0.011 mmol) and $Ph_2P(CH_2)_3CH{=}CH_2$ (**7**) (0.54 g, 1.9 mmol) (ratio 1:200) in benzene (15 cm^3) with H_2/CO (500 psi) at 100 °C for 22 h gave a yellow oil (0.66 g). The ^{31}P and ^1H NMR spectra showed a complex mixture which consisted of two aldehyde isomers **8** and **9** and the internal alcohol **10** in the approximate ratio for **8**:**9**:**10** of 70:11:19. A portion of the crude product (0.39 g) was oxidised as above to give a viscous clear oil which crystallised on standing to give a mixture of 5-diphenylphosphoryl-2-methylpentanoic acid (**12**) and 6-diphenylphosphorylhexanoic acid (**13**) in the ratio 89:11 (0.43 g, 80% based on $Ph_2P(CH_2)_3CH{=}CH_2$). Spectroscopic data: IR (Nujol): ν 2586(br, m), 1703(vs), 1591(w), 1439(s), 1253(m), 1220(m), 1148(vs), 1120(s), 1098(s), 835(m), 810(m), 750(s), 727(s), 697(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (d, 3H, $J_{H2,CH_3} = 6.9$ Hz, CH_3); 1.45–1.87 (m, 10H, H3, H4 (**12**), H3, H4, H5 (**13**)); 2.27–2.49 (m, 3H, H2, H5 (**12**), H2, H5 (**13**)); 7.46–7.77 (m, 20H, 4Ph); 8.06 (br s, 2H, H1 (**12**, **13**)). ^{13}C NMR ($CDCl_3$): δ 17.37 (CH_3), 19.39 (d, $^2J_{PC} = 3.2$ Hz, C4 (**12**)); 21.07 and 24.33 (C3, 4 or 5 (**13**)); 29.30 (d, $^1J_{PC} = 71.6$ Hz, C5 (**12**)); 33.87 (C2 (**13**)); 35.11 (d, $^3J_{PC} = 14.7$ Hz, C3 (**12**)); 128.70 (d, $J_{PC} = 11.9$ Hz); 130.81 (overlapping doublets, $J_{PC} = 11.3$, $J_{PC} = 7.9$ Hz, 2 (C2′, C3′, C5′, C6′ (**12** and **13**)); 132.00 (d, $^1J_{PC} = 99.9$ Hz, C1′ of Ph (**12** and **13**)); 132.11 (d, $^1J_{PC} = 99.9$ Hz, C1′ of Ph (**12** and **13**)); 176.41 (C1 (**13**)); 178.73 (C1 (**12**)). Note that two methylene signals of the minor component **13** were not detected. These are probably degenerate with those of compound **12**. ^{31}P NMR ($CDCl_3$): $\delta + 35.48$; MS, *m/z* (relative intensity): 316 (16%, M^+), 271 (23, $C_{17}H_{20}OP^+$), 229 (17, $C_{14}H_{13}OP^+$), 216 (96, $C_{13}H_{13}OP^+$), 215 ($C_{13}H_{12}OP^+$), 202 (68, $C_{12}H_{11}OP^+$), 201 (75, $C_{12}H_{10}OP^+$), 183 (12, $C_{12}H_8P^+$), 155 (12), 125 (18), 77 (50), 51 (13). The spectral data for acid **12** were identical with those reported above.

Results and discussion

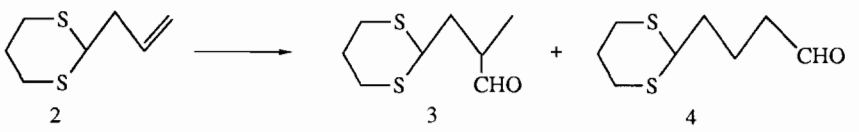
Hydroformylation of styrene, vinyl acetate and allyl acetate

The heterobinuclear catalyst $(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ (**1**) [3] was evaluated as a catalyst for hydroformylation by studying reactions of some typical alkenes. Reaction of styrene was complete after 20 h at 50 °C with a CO/H_2 pressure of 380 psi (2620 KPa) and a catalyst to substrate ratio of *c.* 1:100. These conditions are comparable for many hydroformylations of styrene reported in the literature [1, 13]. Interestingly, the ratio of branched to straight chain aldehydes (98:2) obtained from reaction of styrene is as selective for the branched chain isomer as any reported in the literature [1, 14] for a reaction which gave quantitative conversion.

Reaction of vinyl acetate under the same conditions also gave a quantitative conversion. The aldehydes, 2-acetoxypropanal (branched) and 3-acetoxypropanal (linear) were isolated in high yield (72%) in ratio 75 branched:25 linear. Other literature reports suggest virtual exclusive formation of the branched chain aldehydes [10, 14, 15] unless bulky ligands such as diop were present [16, 17]. Thus the effective size of the catalytic species arising from the bimetallic complex appears to be significant. Conversely, a high proportion of linear aldehyde (89 linear:11 branched) was obtained from reaction of allyl acetate, however the isolated yield of the two aldehydes was not high (*c.* 70%) and other products were formed. Literature reports indicate that hydroformylation of allyl acetate frequently gives complex mixtures, but the ratios of linear to branched aldehydes are usually less than that observed by us [17, 18]. However, Cuny and Buchwald have recently reported a high yield of linear aldehyde using a bulky phosphite ligand in a rhodium catalysed system [19] and Alper and Zhou [20] have reported high linear ratios using a zwitterionic catalyst system.

Reaction of the alkenyldithiane 2

Hydroformylation of the alkenyldithiane **2** has previously been carried out using $Rh_4(CO)_{12}$ as catalyst



2 3 4

at 50 °C as part of a project designed to evaluate the potential regiocontrol that could be exerted by coordination of a remotely substituted ligand atom to the rhodium catalyst in the transition state [11]. A ratio of branched (**3**) to linear (**4**) aldehydes of 84:16 was obtained suggesting that significant regiocontrol was being exerted by the sulfur atoms but that sulfur was not as effective as phosphorus [8] in its directing ability. Reaction using the heteronuclear Rh–W catalyst (**1**) was of interest as it was possible that preferential coordination of the sulfur atoms to tungsten may occur with hydroformylation involving the bonded rhodium atom. Examination of molecular models suggested that should this occur a high preference for the linear aldehyde **4** would result. However, reaction of the dithiane **2** using this catalyst system at 50 °C gave a high yield of aldehydes in ratio 53 (**3**):47 (**4**). Although the proportion of linear aldehyde had significantly increased, the change could be due to the increased steric demands of the bimetallic catalyst system. The sensitivity of the regioselectivity of reactions of the dithiane to steric effects has been demonstrated both by ourselves [11] and more recently by Cuny and Buchwald [19].

Reactions of alkenyl and alkynylphosphines

The bimetallic catalyst **1** was evaluated in hydroformylation reactions of alkenyl (**5**) and (**7**) and alkynyl (**11**) phosphines with chelating geometry related to that of the above dithiane.

$$\underset{\mathbf{5}}{Ph_2P(CH_2)_2CH{=}CH_2} \xrightarrow[[Rh]]{H_2/CO} \underset{\mathbf{6}}{Ph_2P(CH_2)_2\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_3}$$

4-Diphenylphosphinobut-1-ene (**5**) was reacted at 80 °C with 380 psi H_2/CO. The only product, isolated in high yield (*c.* 80%), was the branched chain alcohol (**6**). This result is identical to that obtained using a rhodium acetate/triphenylphosphine catalyst system [8] suggesting that preferential coordination of phosphorus to rhodium rather than to tungsten controls the course of this reaction.

The effect of increasing the distance between the phosphorus atom and the alkene was explored by reacting 5-diphenylphosphinopent-1-ene (**7**). Reaction using the bimetallic catalyst **1** under the same conditions as above gave a quantitative yield of the branched chain aldehyde **8** and the corresponding alcohol **10** in ratio (77:17) together with a small amount (6%) of the linear aldehyde **9**. Reaction using rhodium acetate dimer with or without the addition of small amounts of triphenylphosphine gave similar selectivity of branched to linear products, though the ratio of aldehyde to alcohol was shown to vary in previous work [8].

$$\underset{\mathbf{7}}{Ph_2P(CH_2)_3CH{=}CH_2} \xrightarrow[[Rh]]{H_2/CO}$$

$$Ph_2P(CH_2)_3\underset{\displaystyle CHO}{\underset{|}{C}}HCH_3 + \underset{\mathbf{9}}{Ph_2P(CH_2)_3CH_2CH_2CHO}$$

8

$$Ph_2P(CH_2)_3\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_3$$

10

Rhodium-catalysed hydroformylation of alkynes is usually sluggish compared to reactions of corresponding alkenes. The effect of the bimetallic system on hydroformylation of an alkyne was investigated using 5-diphenylphosphinopent-1-yne, $Ph_2P(CH_2)_3C{\equiv}CH$ (**11**). The reaction of the alkyne **11** at 80 °C (380 psi H_2/CO) was significantly slower than reaction of the corresponding alkene **7** in that only 40% conversion to the internal aldehyde was obtained. A reaction using $[Rh(OAc)_2]_2$ at 100 °C with 500 psi H_2/CO again gave only the internal regioisomers **8** and **10** in ratio 75:25. Conversion was complete under these more forcing conditions and the product mixture was oxidised to give the oxide of the corresponding carboxylic acid in 61% isolated yield. The identical regioselectivity shown for reactions of the alkene **7** and the alkyne **11** is consistent with an initial slow hydrogenation of the alkyne followed by rapid hydroformylation of the resulting alkene as has been suggested previously [21].

Further investigations of the stoichiometric reactions between the Rh–W complex (**1**) and phosphinoalkenes and -alkynes are in progress and will be reported in a subsequent paper.

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