An NMR study of cobalt-catalyzed hydroformylation using *para*-hydrogen induced polarisation[†]

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Received 10th September 2008, Accepted 8th December 2008 First published as an Advance Article on the web 16th February 2009 DOI: 10.1039/b815853c

The syntheses of $Co(\eta^3-C_3H_3)(CO)_2PR_2R'(R, R' = Ph, Me; R, R' = Me, Ph; R = R' = Ph, Cy, CH_2Ph)$ and $Co(\eta^3-C_3H_5)(CO)(L)$ (L = dmpe and dppe) are described, and X-ray structures for $Co(\eta^3-C_3H_3)(CO)(dppe)$ and the PPh₂Me, PCy₃ derivatives reported. The relative ability of $Co(\eta^3-C_3H_5)(CO)_2(PR_2R')$ to exchange phosphine for CO follows the trend PMe₂Ph < PPh₂Me < PCy₃ $< P(CH_2Ph)_3 < PPh_3$. Reactions of the allyl complexes with *para*-hydrogen (*p*-H₂) lead to the observation of *para*-hydrogen induced polarisation (PHIP) in both liberated propene and propane. Reaction of these complexes with both CO and H₂ leads to the detection of linear acyl containing species $Co(COCH_2CH_2CH_3)(CO)_3(PR_2R')$ and branched acyl complexes $Co(COCH(CH_3)_2)(CO)_3$ - (PR_2R') via the PHIP effect. In the case of PPh₂Me, additional signals for Co(COCH₂CH₂CH₃)(CO)₂-(PPh₂Me)(propene) and Co(COCH(CH₃)₂)(CO)₂(PPh₂Me)(propene) are also detected. When the reactions of H_2 and diphenylacetylene are studied with the same precursor, $Co(CO)_3(PPh_2Me)$ -(CHPhCH₂Ph) is seen. Studies on how the appearance and ratio, of the PHIP enhanced signals vary as a function of reaction temperature and H_2 : CO ratio are reported. These profiles are used to learn about the mechanism of catalysis and reveal how the rates of key steps leading to linear and branched hydroformylation products vary with the phosphine. These data also reveal that the PMe₂Ph and PPh, Me based systems yield the highest selectivity for linear hydroformylation products.

Introduction

Cobalt-catalysed alkene hydroformylation represents a reaction that is of significant industrial importance.¹ In this reaction, an alkene reacts with CO and H₂ to form an aldehyde which ideally should correspond to the linear rather than branched isomer. Early catalysts were based on $Co_2(CO)_8$ and proposed to yield $HCo(CO)_4$ under the normally employed reaction conditions.² This "unmodified" system was improved on by replacing a CO for phosphine (modified) because higher linear to branched product ratios resulted; their rhodium based counterparts have become even more important because of their greater selectivity.

Early studies by Heck and Breslow led to an accepted mechanism for the hydroformylation reaction that involves a monohydride precursor which ultimately yields a metal acyl intermediate that eliminates the aldehyde after reaction with H₂. This reaction sequence is indicated in Scheme 1 and operates at temperatures close to 150 °C with combined CO–H₂ pressures of around 200 atmospheres.³ The detection and characterization of the key species involved in this process has proved to be complex, with examples of cobalt acyl and alkyl resting states being isolated.⁴⁻⁶ The unmodified species CH₃C(O)Co(CO)₄, CH₃C(O)Co(CO)₃ and CH₃Co(CO)₄ have also been characterised in low temperature matrices, with the 16-electron species showing little reactivity



Scheme 1 Heck and Breslow hydroformylation mechanism for a modified catalyst, PR₃, showing origin of linear/branched selectivity.

towards other ligands resulting in a proposed η^2 -acyl bonding mode.⁷ Roe has used high pressure NMR methods to demonstrate that the thermal loss of CO from CH₃C(O)Co(CO)₄ has a Gibbs free energy of activation of *ca.* 90 kJ mol⁻¹ at 363 K and

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[†] Electronic supplementary information (ESI) available: NMR and X-ray details. CCDC reference numbers 701811–701813. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b815853c

a rate of 11.5 s⁻¹ at 353 K.⁸ Others have used time-resolved IR studies to show that the η^2 -acyl containing intermediate CH₃C(O)Co(CO)₂(PPh₃) re-coordinates CO at a rate of 1.1 × 10⁷ dm³ mol⁻¹ s⁻¹ while undergoing competitive decarbonylation of the acyl ligand at a rate of 6.2×10^4 s⁻¹ at 25 °C.⁹

Studies on the thermal reactivity of $CH_3CH_2CH_2Co(CO)_3$ -(PBu₃) revealed the formation of $HCo(CO)_3(PBu_3)$, $[Co(CO)_3(PBu_3)]_2$ and $CH_3CH_2CH_2C(O)Co(CO)_3(PBu_3)$ in addition to H_2 and propene at 40 °C.¹⁰ Similar studies on $(CH_3)_2CHCo(CO)_3$ -(PBu₃) were also described and Rosi *et al.* concluded that the isomerisation of these species under standard hydroformylation conditions does not justify the product mix obtained when $Co_2(CO)_8$ –PBu₃ is itself examined. The hydroformylation reactions selectivity was therefore suggested to result from the regioselectivity of CoH group transfer to the bound alkene.

A more complete picture of the hydroformylation of propene by $HCo(CO)_4$ has been assembled from density functional theory.¹¹⁻¹³ The most stable alkene hydride complex, $HCo(CO)_3(CH_2=CHMe)$, was found to contain an axial hydride ligand and equatorial alkene. Subsequent hydride transfer proved to be reversible, with the regioselectivity being found to be mainly determined by the stability of the corresponding alkylcobalt tetracarbonyl product. In the presence of CO, the formation of the unsaturated, η^2 -stabilised acyls, $(CH_3)_2CHC(O)Co(CO)_3$ and $CH_3CH_2CH_2C(O)Co(CO)_3$ was indicated. Reactions of these species with H₂ were then considered to proceed *via* simple and reversible H₂ coordination rather than oxidative addition, which was shown to correspond to a high-energy product on the way to aldehyde formation.^{11,12}

The formation of π -allyl cobalt containing complexes has been shown to be possible *via* reactions of anions such as Co(CO)₄⁻ with allylbromide,¹⁴ or *via* allyl transfer from chloro-allyl palladium dimers.¹⁵ Furthermore, the reaction of the allyl cobalt complex (η^3 -C₃H₅)Co(CO)₂PPh₃ with PPh₃ and HSiMe₂Ph has been shown to enable the formation of Co(CO)₂(PPh₃)₂(SiMe₂Ph) with the concomitant formation of propene.¹⁶ This corresponds to an elegant route to the formation of a cobalt–silyl complex. When such compounds react with H₂, however, the formation of paramagnetic clusters such as [Co(CO)₂(PPh₃)]₃ has been previously described.¹⁷ These clusters are produced by the trimerisation of CoH(CO)₂(PPh₃) and result in H₂ generation. Such systems have also been found to be active as arene hydrogenation catalysts.¹⁸

In this paper we describe studies that employ $Co(\eta^3 - \eta^3)$ $C_{3}H_{5}(CO)_{2}PR_{2}R'(R, R' = Ph, Me; R, R' = Me, Ph; R = R' = Ph,$ Cy, CH₂Ph) as precursors to study cobalt based hydroformylation by NMR spectroscopy. These studies have also involved the use of para-hydrogen (p-H₂).¹⁹ p-H₂ has been used, because it leads to the observation of the PHIP (para-hydrogen induced polarisation)²⁰ effect. This effect has enabled the direct NMR detection of metal hydride signals for complexes in solution that would otherwise be invisible.²¹ PHIP NMR spectroscopy has also been shown to permit the direct identification of metal complexes without the need for enhancement of metal hydride signals, an example being the characterization of intermediates in palladium-catalyzed hydrogenation through proton resonances of alkyl ligands.²² This paper builds on a communication where the reactivity of $Co(\eta^3-C_3H_5)(CO)_2(PCy_3)$ was described.²³ We have employed temperatures up to 120 °C but our highest total pressure is 4 atm.

Experimental

General conditions

All manipulations were carried out under inert atmosphere conditions, using standard Schlenk techniques (vacuum up to 10^{-2} mbar, with N₂ as an inert atmosphere) or high vacuum techniques (10^{-4} mbar). Storage and manipulation of samples were carried out using standard glovebox techniques, under an atmosphere of N₂, using an Alvic Scientific Gas Shield glovebox equipped with a freezer (-32 °C), vacuum pump and N₂ purge facilities. Solvents were obtained as Analytical Grade from Fisher, and dried when appropriate by refluxing under nitrogen over sodium wire.

X-Ray data were obtained using a Bruker Smart Apex diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using "SMART" (v5.625 Bruker-AXS).²⁴ Frame integration and unit-cell refinement was carried out with the "SAINT+" software (v6.22, Bruker AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick).

The syntheses of the cobalt allyl complexes described in this paper were carried out using modified literature procedures as detailed below.^{25,26}

Synthesis of Co(η³-C₃H₅)(CO)₂(PPh₂Me) 1

 $Co(CO)_4$ Na was prepared by reduction of $Co_2(CO)_8$ (0.6 g, 1.7 mmol) in 100 ml of THF by NaOH powder (ca. 1 g, large excess) in the glovebox. The solution was stirred for 30 minutes at room temperature and the colourless solution was then filtered. Addition of 0.4 ml (27 mmol, large excess) of freshly distilled allybromide to the eluant was performed at 0 °C and the resulting solution stirred at this temperature for ca. 30 minutes before being allowed to warm up to room temperature. After 15 minutes, the colour of the solution had turned bright yellow due to the formation of $Co(\eta^3-C_3H_5)(CO)_3$. A THF solution (20 ml) containing a slight excess of PPh₂Me (700 µl, 3.75 mmol, 1.1 eq.) was then slowly added via cannula transfer and the reaction mixture stirred at room temperature for 15-20 minutes. The orange solution was then filtered, and the solvent removed under vacuum. Extraction in pentane yielded a dark orange-red solution. Purification was performed by precipitation in pentane at -80 °C, filtration and the recrystallisation of the precipitate from diethylether. Yield = 420 mg, 34%. v_{co} in CH₂Cl₂ (cm⁻¹) 1983, 1923.

The syntheses of $Co(\eta^3-C_3H_3)(CO)_2(PPhMe_2)$ **2**, $Co(\eta^3-C_3H_3)-(CO)_2(P(CH_2Ph)_3)$ **3**, $Co(\eta^3-C_3H_5)(CO)_2(PCy_3)$ **4** and $Co(\eta^3-C_3H_5)(CO)_2(PPh_3)$ **5** are described in the ESI.†

Synthesis of $Co(\eta^3-C_3H_5)(CO)_2(dppm)$ (dppm = diphenyphosphinomethane) 6

A THF solution of $Co(\eta^3-C_3H_5)(CO)_3$ (3.4 mmol) was prepared as described above for **1**. A THF solution (20 ml) containing a slight excess of dppm (1.4 g, 3.75 mmol, 1.1 eq.) was then slowly added *via* cannula transfer and the reaction mixture stirred at room temperature for 15–20 minutes. The orange solution was then filtered, and the solvent removed under vacuum. Purification of the product was carried out by recrystallisation from a dichloromethane solution. Yield = 55%.

Synthesis of $Co(\eta^3-C_3H_5)(CO)(dppe)$ (dppe = diphenyphosphinoethane) 7

A THF solution of $Co(\eta^3-C_3H_5)(CO)_3$ (3.4 mmol) was prepared as described above for **1**. A THF solution (20 ml) containing a slight excess of dppe (1.5 g, 3.75 mmol, 2.2 eq.) was then slowly added *via* cannula transfer and the reaction mixture stirred at room temperature for 12 hours. The orange solution was then filtered, and the solvent removed under vacuum. The orange solid was then re-dissolved in the minimum amount of THF and precipitated by addition of pentane, filtration and washing of the remaining solid with pentane. Yield = 30%. v_{CO} in CH₂Cl₂ (cm⁻¹) 1925.

para-Hydrogen

For the PHIP experiments, hydrogen enriched in the *para* spin state was prepared by cooling H₂ to 18 K over a paramagnetic catalyst (Fe₂O₃ on silica) using the system described previously.²⁷ All the NMR studies were carried out with sample concentrations of approximately 1 mM and spectra were recorded on a Bruker DRX-400 spectrometer with ¹H at 400.1, ³¹P at 161.9 and ¹³C at 100.0 MHz, respectively. ¹H NMR chemical shifts are reported in ppm relative to residual ¹H signals in the deuterated solvents (toluene-d₇, δ 2.13, and C₆D₅H, δ 7.16), ¹³C NMR relative to toluene-d₈, δ 21.3 and C₆D₆, δ 128.4 and ³¹P NMR in ppm downfield of an external 85% solution of phosphoric acid. Modified COSY, HMQC and EXSY pulse sequences were used as previously described.^{28,29}

Results and discussion

Syntheses of $Co(\eta^3-C_3H_3)(CO)_2PR_2R' 1-5$ (R, R' = Ph, Me; R, R' = Me, Ph; R = R' = Ph, Cy, CH, Ph)

The Co(η^3 -C₃H₅)(CO)₂PR₂R' complexes **1–5** where R, R' = Ph, Me (1); R, R' = Me, Ph (2), and R = R' = CH₂Ph (3), Cy (4) and Ph (5) were prepared from *in situ* generated Co(η^3 -C₃H₅)(CO)₃ which was obtained from the reaction of Co(CO)₄Na with allylbromide.²⁵ Room temperature addition of a small excess of the appropriate phosphine to Co(η^3 -C₃H₅)(CO)₃ led to the desired products, Co(η^3 -C₃H₅)(CO)₂(PR₂R'), in good yield (Scheme 2). Complexes **1–5** have been characterized by mass spectrometry, and IR and NMR spectroscopy (Table 1 and experimental). In addition, crystals of **1** (PPh₂Me) that were suitable for X-ray analysis were



Scheme 2 Synthesis of $Co(\eta^3-C_3H_5)(CO)_2PR_2R'$, where R, R' = Ph, Me (1); R, R' = Me, Ph (2); R = R'= CH_2Ph (3), Cy (4), and (5) Ph.

obtained by slow evaporation of a diethylether solution, while crystals of **4** (PCy₃) were obtained from toluene as described previously.²³

ORTEP representations of the structures of **1** and **4** are shown in Fig. 1. The structures of these species are similar to that of the previously reported $Co(\eta^3-C_3H_5)(CO)_2(PPh_3)$ **5** analogue²⁶ and can be described as piano stools with capping η^3 -allyl ligands. The piano stool includes the $Co(CO)_2(PR_2R)$ moiety, where in the case of PPh₂Me, the Co–P bond length is 2.1715(7) Å and the two distinct Co–C(O) bond lengths are 1.772(3) Å and 1.757(3) Å. The corresponding Co–P bond length in **4** is 2.2190(4) Å, and the Co–C(O) distances are almost identical at 1.7812(14) Å and 1.7592(14) Å. The reported Co–PPh₃ distance in **5** is 2.185 Å, and again almost identical to the corresponding distance in **1**.

The C-Co-C angle in 1 (R = Ph, Me) was found to be 116.52(13)°, while the C-Co-P angles were found to be smaller at 99.65(9)° and 96.05(9)°. The matching angles in 4 (R = Cy) are, however, 107.73(7)°, 95.12(5)° and 104.39(5)° respectively²³ while those for 5 (R = Ph) are reported as being $111.3(2)^{\circ}$, $93.0(1)^{\circ}$ and 104.7(1)° respectively. This is consistent with the relative cone angles of the phosphine controlling the resulting geometry.³⁰ In other words, the C-Co-C angle becomes compressed as the structure changes to reflect the steric effect of the phosphine. The Co- C_{allvl} distances in 1 were found to be 2.093(3) Å, 2.016(3) Å and 2.119(3) Å, and similar to those found for 5 while the corresponding Co– C_{allvl} distances for 4 are 2.0841(15) Å, 2.0074(14) Å and 2.1197(14) Å respectively. There is therefore no discernable trend in the Co-Callyl distance across the series of compounds. The two C-C bond lengths within the allyl ligand of 1 were determined to be 1.416(4) Å and 1.364(4) Å, while those of 5 were reported as 1.399(7) Å and 1.385(8) Å, and those of 4 are 1.410(2) Å and 1.397(2) Å. The analogous CO distances for



Fig. 1 ORTEP diagrams of (a) $Co(\eta^3-C_3H_5)(CO)_2(PPh_2Me)$ 1, (b) $Co(\eta^3-C_3H_5)(CO)_2(PCy_3)$ 4 and (c) $Co(\eta^3-C_3H_5)(CO)(dppe)$ 7. Ellipsoids drawn at 50% probability level.

		Hb ≞	
		Hc Ha	
		$K K_2 r'/h_{h_{1}} \checkmark$	
Species	¹ H δ (multiplicity, intensity)	¹³ C{ ¹ H}	³¹ P{ ¹ H}
1	4.47 (tt, 1H) H _a , $J_{HH} = 6$ and 11 Hz 2.44 (dd, 2H) H _b (<i>anti</i>), $J_{HH} = 6$ Hz, $J_{HP} = 4$ Hz 1.88 (d, 2H) H _c (<i>syn</i>), $J_{HH} = 11$ Hz 1.63 (d, 3H) PMePh ₂ , $J_{HP} = 8$ Hz 7–7.5 (m) PMePh ₂	205.2 (br) CO 80.0 (s) CH allyl 46.0 (s) CH ₂ allyl 19.4 (d) PMePh ₂ , $J_{PC} = 29$ Hz 120–135 (m) PMePh ₂	43.8 (s)
2	4.46 (tt, 1H) H_a , $J_{HH} = 6$ and 11 Hz 2.35 (dd, 2H) H_b (<i>anti</i>), $J_{HH} = 6$ Hz, $J_{HP} = 4$ Hz 1.83 (d, 2H) H_c (<i>syn</i>), $J_{HH} = 11$ Hz 1.28 (d, 6H) PMe_2Ph , $J_{HP} = 8$ Hz 7–7.8 (m) PMe_2Ph	197.6 (br) CO 79.5 (s) CH allyl 45.05 (s) CH ₂ allyl 19.2 (d) PMe_2Ph , $J_{PC} = 29$ Hz 120–140 (m) PMe_2Ph	28.0 (s)
3	4.22 (tt, 1H) H _a , $J_{\text{HH}} = 6$ and 10.5 Hz 2.11 (m, 2H) H _b (<i>anti</i>) 1.58 (d, 2H) H _c (<i>syn</i>), $J_{\text{HH}} = 10$ Hz 2.91 (d, 6H) P(<i>CH</i> ₂ Ph) ₃ , $J_{\text{HP}} = 9$ Hz 7–7.2 (m) P(CH ₂ Ph) ₃	204.5 (d) CO, $J_{PC} = 8$ Hz 82.0 (s) CH allyl 44.2 (d) CH ₂ allyl, $J_{PC} = 3$ Hz 38.6 (d) P(CH ₂ Ph) ₃ , $J_{PC} = 17$ Hz 125–140 (m) P(CH ₂ Ph) ₃	63.9 (s)
4	4.78 (tt, 1H) H_a , $J_{HH} = 6$ and 10.5 Hz 2.61 (dd, 2H) H_b (<i>anti</i>), $J_{HH} = 6$ Hz, $J_{HP} = 3$ Hz 1.82 (d, 2H) H_c (<i>syn</i>), $J_{HH} = 10.4$ Hz 1.0–2.0 (m) PCy ₃	208 (d) CO, $J_{PC} = 8$ Hz 79.4 (s) CH allyl 43.4 (s) CH ₂ allyl 25–40 (m) PCy ₃	69.1 (s)
6	4.31 (m, 1H) H _a 2.61 (dd, 2H) H _b (<i>anti</i>), $J_{HH} = 5$ Hz, $J_{HP} = 4$ Hz 1.87 (d, 2H) H _c (<i>syn</i>), $J_{HH} = 10$ Hz 3.16 (br) Ph ₂ P–CH ₂ –PPh ₂ 6–8 (m) Ph_2 P–CH ₂ –PPh ₂	206.7 (br) CO 80.3 (s) CH allyl 46.8 (s) CH ₂ allyl 34.1 (dd) Ph ₂ P–CH ₂ –PPh ₂ , $J_{PC} = 22$ and 32 Hz 120–140 (m) Ph_2 P–CH ₂ –PPh ₂	53.0 (br d), <i>J</i> _{PP} = 98 Hz -26.1 (d), <i>J</i> _{PP} = 98 Hz
7	4.32 (m, 1H) H_a 2.50 (m, 2H) H_b (<i>anti</i>) 1.90 (m, 2H) H_c (<i>syn</i>) 2.61 (d) $Ph_2P-(CH_2)_2-PPh_2$ 6-8 (m) $Ph_2P-CH_2-PPh_2$	207.0 (br) CO 90.0 (s) CH allyl 47.1 (s) CH ₂ allyl 27.6 (dd) Ph ₂ P–(CH ₂) ₂ –PPh ₂ , $J_{PC} = 14$ and 28 Hz 120–140 (m) Ph_2P –(CH ₂) ₂ –PPh ₂	58.5 (s)

 Table 1
 NMR data for complexes 1–4 and 6–7 in toluene-d₈ solution at 295 K

1 are 1.146(3) and 1.146(3) while those of **5** are 1.141(4) Å and 1.139(6) Å and those of **4**, are 1.1513(18) Å and 1.1522(18) Å.

These data suggest that neither the Co–CO nor the allyl CH_2 –CH distances change substantially with change in electron donating power of the phosphine. Key distances and bond angles for 1 are listed in Table 2 while those for 4 can be found in ref. 23. Crystal parameters are listed in Table 3.

Synthesis of Co(η^3 -C₃H₅)(CO)₂(PPh₂CH₂PPh₂) 6 and Co(η^3 -C₃H₅)(CO)(PPh₂CH₂CH₂PPh₂) 7

The syntheses of the related complexes containing the chelating phosphines bisdiphenylphosphinomethane, $Co(\eta^3-C_3H_3)(CO)_2(dppm)$ **6**, and bisdiphenylphosphinoethane, $Co(\eta^3-C_3H_3)(CO)(dppe)$ **7** were also completed. The reaction with dppm proved to readily yield a dicarbonyl complex where the phosphine ligand is coordinated through only one phosphorus centre. When a solution of dppe was added slowly to a dilute solution of $Co(\eta^3-C_3H_3)(CO)_3$, however, the main product proved to be $Co(\eta^3-C_3H_3)(CO)(dppe)$ **7** where the dppe ligand is chelating. These complexes have also been characterized by mass spectrometry, IR and NMR spectroscopy (see Table 1).

Table 2 Selected bond lengths (Å) and angles (°) for $Co(\eta^3\text{-}C_3H_5)\text{-}(CO)_2(PPh_2Me)\,1$

Assignment	Value	Assignment	Value
Co(1)–P(1)	2.1715(7)	C(3)-Co(1)	2.093(3)
C(1) - O(1)	1.146(3)	C(4) - Co(1)	2.016(3)
C(1) - Co(1)	1.772(3)	C(5) - Co(1)	2.119(3)
C(2) - O(2)	1.146(3)	C(3) - C(4)	1.416(4)
C(2)–Co(1)	1.757(3)	C(4) - C(5)	1.364(4)
O(1)-C(1)-Co(1)	177.6(3)	C(2)-Co(1)-C(1)	116.52(13)
O(2) - C(2) - Co(1)	178.4(2)	C(2)-Co(1)-C(4)	101.56(13)
C(4)-C(3)-Co(1)	66.91(16)	C(1)-Co(1)-C(4)	125.41(13)
C(3)-C(4)-Co(1)	72.82(16)	C(2)-Co(1)-C(3)	92.32(12)
C(5)-C(4)-C(3)	116.5(3)	C(1)-Co(1)-C(3)	98.06(12)
C(5)-C(4)-Co(1)	74.92(18)	C(4)-Co(1)-C(3)	40.27(12)
C(4)-C(5)-Co(1)	66.67(17)	C(2)-Co(1)-C(5)	135.39(14)
C(1)-Co(1)-P(1)	99.65(9)	C(1)-Co(1)-C(5)	106.05(15)
C(4)-Co(1)-P(1)	114.23(9)	C(4)-Co(1)-C(5)	38.41(12)
C(3)-Co(1)-P(1)	154.46(8)	C(3)-Co(1)-C(5)	68.26(12)
C(5)–Co(1)–P(1)	89.16(10)	C(2)-Co(1)-P(1)	96.05(9)

Crystals of 7 suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution, and the corresponding ORTEP diagram is shown in Fig. 1(c). It should be noted, that it has

Table 3 Crystal data and structure refinement information for 1, 7 and $[Co(CO)_3PPh_3]_2$

Complex	1	7	[Co(CO) ₃ PPh ₃] ₂
Empirical formula	$C_{18}H_{18}CoO_2P$	$C_{30}H_{29}CoOP_2$	$C_{21}H_{15}CoO_3P$
Formula weight	356.22	526.40	405.23
Temperature/K	388(2)	115(2)	393(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Rhombohedral
Space group	Pbca	PĪ	RĪ
a/Å	15.2928(17)	9.4425(7)	15.2724(19)
b/Å	13.6440(16)	9.4559(6)	15.2724(19)
c/Å	15.9287(18)	14.7071(10)	13.854(4)
$\alpha /^{\circ}$	90	93.077(2)	90
β/°	90	104.880(2)	90
$\gamma/^{\circ}$	90	101.761(2)	120
Volume/Å ³	3323.6(7)	1234.65(15)	2798.5(9)
Ζ	8	2	6
Density (calculated)/Mg m ⁻³	1.424	1.416	1.443
Absorption coefficient/mm ⁻¹	1.132	0.846	1.022
F(000)	1472	548	1242
Crystal size/mm ³	$0.3 \times 0.2 \times 0.1$	$0.21 \times 0.11 \times 0.05$	$0.19 \times 0.18 \times 0.02$
θ range for data collection/°	2.37 to 30.98	1.44 to 25.03	2.13 to 25.01
Index ranges	$-22 \leqslant h \leqslant 21, -19 \leqslant k \leqslant 18,$	$-11 \leqslant h \leqslant 5, -11 \leqslant k \leqslant 11,$	$-18 \leqslant h \leqslant 18, -18 \leqslant k \leqslant 17,$
	$-22 \leqslant l \leqslant 22$	$-16 \leq l \leq 17$	$-16 \leq l \leq 16$
Reflections collected	35594	7070	6523
Independent reflections	$5049 [R_{int} = 0.0696]$	$4325 [R_{int} = 0.0211]$	$[1091 [R_{int} = 0.0342]]$
Completeness to $\theta = 30.98^{\circ}$ (%)	95.5	99.0	99.2 S
Absorption correction	Multi-scan	0.060 and 0.822	1 000 and 0 785
Max. and min. transmission	1.000 and 0.824	0.960 and 0.822	1.000 and 0.785
Data /restraints /parameters	5049 /0 /200	1325/0/307	1001/0/79
Goodness-of-fit on F^2	1 061	1 033	1 110
Final R indices $[I > 2\sigma(I)]$	$R_{\rm c} = 0.0511 \text{ w} R_{\rm c} = 0.1133$	$R_1 = 0.0343 \text{ w} R_2 = 0.0827$	$R_1 = 0.0242$, w $R_2 = 0.0671$
R indices (all data)	$R_1 = 0.0736$, w $R_2 = 0.1227$	$R_1 = 0.0461, wR_2 = 0.0874$	$R_1 = 0.0261, wR_2 = 0.0679$
Largest diff. peak and hole/e Å ⁻³	1.234 and -0.384	0.587 and -0.607	0.339 and -0.293

previously been reported that reactions of $Co(\eta^3-C_3H_3)(CO)_3$ with dppe, led to $Co(\eta^3-C_3H_5)(CO)(dppe)$ and $[Co(\eta^3-C_3H_5)(CO)_2](\mu$ -dppe).³¹ We have found that increasing the concentrations of $Co(\eta^3-C_3H_5)(CO)_3$ relative to dppe yields the dimeric species $[Co(\eta^3-C_3H_5)(CO)_2(\mu$ -dppe)]_2 and that $Co(\eta^1-C_3H_5)(CO)_2(dppe)$ can be readily obtained by addition of the dppe to $Co(\eta^1-C_3H_5)(CO)_4$ at 0 °C.

The bisphosphine substituted species 7 also exhibits a piano stool geometry with a capping η^3 -allyl ligand. The piano stool moiety is defined by the metal, the carbonyl ligand and the two phosphorus centres. The corresponding Co–C and Co–P bond lengths were found to be 1.770(3), 2.1640(7) and 2.1709(7) Å respectively and are almost identical to those seen for 1. The Co–C_{allyl} bond lengths of 7 are 1.987(3), 1.987(3) and 2.082(3) Å and therefore slightly shorter than those seen for both 1 and 4. The C–C bonds for the allyl ligand at 1.413(4) and 1.417(4) Å are, however, still similar to those of 1 and 4. Key distances and bond angles for 7 are listed in Table 4.

Reactivity of 1–7 towards H₂

When a toluene-d₈ solution of $Co(\eta^3-C_3H_3)(CO)_2(PPh_2Me)$ **1** is placed under 3 atm of *p*-H₂ at 295 K and monitored by ¹H NMR spectroscopy, the observation of *p*-H₂ enhanced signals for propane at $\delta 0.9$ (t, $J_{HH} = 7$ Hz) and $\delta 1.305$ (doublet of antiphase triplets where the separations are 7 and 22 Hz respectively) is immediately apparent. On warming to 308 K additional *p*-H₂

Table 4 Selected bond lengths (Å) and angles (°) for Co($\eta^3-C_3H_5)(CO)(dppe)$ 7

Assignment	Value	Assignment	Value
Co(1)-C(1)	1.770(3)	O(1)–C(1)	1.150(3)
Co(1) - P(1)	2.1640(7)	C(3) - C(2)	1.413(4)
Co(1) - P(2)	2.1709(7)	C(3) - C(4)	1.417(4)
Co(1) - C(2)	2.084(3)	C(5) - P(1)	1.869(2)
Co(1) - C(3)	1.987(3)	C(5) - C(6)	1.529(3)
Co(1) - C(4)	2.082(3)	P(2)–C(6)	1.838(2)
O(1)-C(1)-Co(1)	178.6(2)	C(6)–P(2)–Co(1)	104.71(8)
P(1)-Co(1)-P(2)	85.06(3)	C(5) - P(1) - Co(1)	110.06(8)
C(1)-Co(1)-C(3)	128.64(11)	C(2)-Co(1)-P(1)	92.05(8)
C(1) - Co(1) - C(4)	102.12(11)	C(6) - C(5) - P(1)	109.25(16)
C(1)-Co(1)-C(2)	104.84(11)	C(3)-Co(1)-P(2)	114.63(8)
C(1) - Co(1) - P(1)	107.89(9)	C(4) - Co(1) - P(2)	98.66(7)
C(1)-Co(1)-P(2)	102.69(8)	C(2)-Co(1)-P(2)	151.84(8)
C(2)-C(3)-C(4)	114.9(2)	C(5)-C(6)-P(2)	107.59(16)
C(3) - Co(1) - C(2)	40.53(10)	C(3) - C(4) - Co(1)	66.07(14)
C(3)-Co(1)-P(1)	109.22(8)	C(3)-C(2)-Co(1)	66.06(14)
C(4)-Co(1)-P(1)	148.17(7)	C(4)-Co(1)-C(2)	69.86(10)

enhanced signals for propene become visible in the associated $^1\mathrm{H}$ NMR spectra.

The observation of p-H₂ enhanced signals for free propene and propane requires that Co(η^3 -C₃H₅)(CO)₂(PPh₂Me) **1** not only adds H₂, but that hydrogen transfer to the allyl functionality follows such that two protons of a single p-H₂ molecule become located in the liberated ligand. In the case of the iridium analogue of $Co(\eta^3-C_3H_5)(CO)_2(PPh_2Me)$, $Ir(\eta^3-C_3H_5)(CO)(PPh_3)_2$, the detection of the H₂ addition product $Ir(\eta^3-C_3H_5)(CO)(PPh_3)(H)_2$ was facilitated by *p*-H₂ enhanced NMR methods.³² This supports the suggestion that the short lived intermediate $Co(\eta^3-C_3H_5)(CO)(PPh_2Me)(H)_2$, or its analogous η^2-H_2 form, is produced in this reaction, even though it is not directly observed.

It is also logical to assume that hydride transfer to form $Co(CO)_2(PPh_2Me)(propene)(H)$ takes place. This process places one *p*-H₂ derived proton on the methyl group, while leaving one behind as a hydride ligand on the metal. In order to account for the observation of *p*-H₂ enhanced propene and propane signals, this species must undergo, a further reversible, [1,3]-hydride shift to exchange a non-enhanced proton of the propene ligand for the remaining *p*-H₂ derived hydride ligand. This process can occur *via* hydride transfer to form a linear or branched alkyl as shown in Scheme 3. The appearance of the ¹H NMR signals for the liberated propene should therefore reveal information about this combination of steps.



Scheme 3 Hydrogen transfer pathways indicated *via* the observed polarisation profiles for a route involving $Co(\eta^3-C_3H_5)(CO)PR_2R'(H)_2$; this would be equally valid for $Co(\eta^3-C_3H_5)(CO)PR_2R'(H_2)$.

Fig. 2(a) illustrates the vinyl region of such a ¹H NMR spectrum, with each of the three vinyl proton locations showing $p-H_2$ enhanced features. The potential for hydride–hydrogen exchange means that the two protons that were originally in $p-H_2$ might find themselves in a variety of positions in the propene product. The experimental spectrum therefore corresponds to the sum of these individual arrangements. Fig. 2(b)–(g) illustrate appropriate NMR spectral simulations³³ for the vinyl proton resonances of propene, where the $p-H_2$ derived protons are present in the indicated sites. Collectively it can been seen that the spectral trace associated with Fig. 2(a) corresponds to the summation of simulated traces b, c, e, f and g. Trace b arises from the situation where the $p-H_2$ based protons are located *cis* to one another, trace c where they are *trans*, and traces e, f and g are produced when one $p-H_2$ derived proton



Fig. 2 (a) ¹H NMR spectrum of the vinyl region of p-H₂ enhanced propene at 308 K. (b) NMR simulation for p-H₂ based protons at sites b and c. (c) NMR simulation for p-H₂ based protons at sites a and c. (d) NMR simulation for p-H₂ based protons at sites a and b. (e) NMR simulation for p-H₂ based protons at sites c and d. (f) NMR simulation for p-H₂ based protons at sites a and d. (g) NMR simulation for p-H₂ based protons at sites b and d.

is in a methyl group and the other in one of the vinyl sites. The simulations suggest that in order to reproduce the appearance of the alpha proton resonance shown in Fig. 2(a), traces b, c, e, f and g need to be summed together in an approximate ratio of 1.75:2:1:1.75:1.

The proton arrangement necessary to obtain trace e can be obtained by migration to form a linear alkyl, followed by β -H transfer back to the metal prior to alkene loss, while traces f and g can be obtained from a branched alkyl followed by a β -H transfer back to the metal. The first step in this sequence, the transfer of a metal hydride to an allyl terminus has been observed previously.34 Traces b and c are obtained by placing a proton from $p-H_2$ on the central carbon with the second proton being located on one of the geminal sites. This can be easily achieved if the original hydride transfer in $Co(\eta^3-C_3H_5)(CO)(PPh_2Me)(H)_2$ proceeds to the central carbon atom of the allyl, otherwise it requires multiple rearrangements. The missing permutation, where a and b (the two geminal sites) are both occupied, requires multiple rearrangements regardless of the site of the initial proton transfer and is therefore less probable. The transfer of a hydride to the central carbon of an allyl ligand has precedent.35

Complex (PR ₂ R')	Propane appearance temperature/K	Propene appearance temperature/K
1 (PPh ₂ Me)	295	308
$2 (PMe_2Ph)$	303	308
$3(P(CH_2Ph)_3)$	318	323
4 (PCy ₃)	333	333
5 (PPh ₃)	323	328
6 (dppm)	313	318
7 (dppe)	318	323

Only at temperatures above 308 K does propene liberation from $Co(CO)_2(PPh_2Me)(propene)(H)$ become competitive with propane formation. There is, however, a substantial difference in appearance of the signals for propene at temperatures above 373 K. This change is consistent with an increase in the degree of hydride transfer to the central carbon.

The trapping of either of the proposed 16-electron cobalt alkyl intermediates, $Co(CH_2CH_2CH_3)(CO)_2(PPh_2Me)$ or $Co(CH_2(CH_3)_2)(CO)_2(PPh_2Me)$, that are formed by the second [1,3]-hydride shift, with a second H₂ molecule and subsequent reductive elimination of the alkane accounts for the enhanced propane resonances that are seen in these NMR spectra.

Analogous observations were made when the addition of H₂ to complexes 2-7 was studied in a similar way. In fact, the appearance of the propene ¹H NMR signals proved to be similar regardless of the identity of the phosphine. The only significant difference observed in the reactivity of complexes 1-7 towards H₂ stems from the temperature needed to see enhanced propene signals. Table 5 summarizes this information as a function of the complex. In all cases, the observation of p-H₂ enhanced signals for propane occurred at lower temperatures than those required for the observation of propene. This confirms that the addition of H₂ to the alkyl complex, formed by hydride migration onto the bound propene, and the associated reductive elimination of propane, proceeds more rapidly than the combination of the two steps, β -H transfer and alkene liberation, which are necessary to see enhanced signals for free propene. In addition, these data also suggest that $Co(\eta^3-C_3H_5)(CO)_2(PCy_3)$ 4 undergoes the least effective allyl hydrogenation.

The production of propene and propane must coincide with the destruction of the starting complex $Co(\eta^3-C_3H_5)(CO)_2PR_2R'$. Consequently it is not surprising that in the associated NMR spectra, hydride resonances indicative of the formation of $Co(H)(CO)_3(PR_2R')$ and $Co(H)(CO)_2(PR_2R')_2$ were also seen at the end of the experiments.³⁶

The formation of an allyl hydride complex from a metal propene complex is exemplified by the chemistry of $W(CO)_4(\eta^2-C_3H_6)_2^{37}$ Fe(CO)₄($\eta^2-C_3H_6$)³⁸ and Cp*Re(CO)₂($\eta^2-C_3H_6$).³⁹ In order to test whether the first hydride migration to the allyl ligand in Co($\eta^3-C_3H_5$)(CO)(PR₂R')(H)₂ is reversible, a sample of **4** was prepared and placed under a 1:2 mixture of propene and *p*-H₂. ¹H NMR spectra recorded at 363 K revealed enhanced signals for propane, but complex **4** still proved to be rapidly consumed and the formation of the known complexes Co(H)(CO)₃(PCy₃) and Co(H)(CO)₂(PCy₃)₂ indicated. This suggests that the corresponding intermediates are not stabilized

and that $Co(CO)_2(PCy_3)$ (propene)(H) is unable to re-form the initial dihydride allyl complex which would lead, in turn, to the reformation of **4** after H₂ loss. It should be noted that it has been suggested that such a process is reversible for $Co(P(OMe)_3)_2(H)(CH_2=CHCH_2Ph)$ and that a dihydride form is accessed.⁴⁰

Reactivity of complexes 1-5 towards CO

Prior to examining the hydroformylation activity of these systems, a series of control experiments were undertaken where a number of toluene-d₈ based samples were prepared for each of the complexes and exposed to an atmosphere of CO. When the solution of 1 was examined, ${}^{31}P{}^{1}H$ NMR spectroscopy revealed the liberation of PPh₂Me, while the associated ¹H NMR spectrum confirmed the formation of a new η^3 -allyl complex. This complex was subsequently identified as $Co(\eta^3-C_3H_5)(CO)_3$.^{25,41} Similar results were obtained for all the phosphines except PMe₂Ph which did not react at room temperature. Interestingly, no evidence for the insertion of CO into an η^1 -allyl ligand was evident in any of the NMR spectra recorded between 213 K or 383 K. This contrasts with the situation that has been reported for $Ir(CO)(PPh_3)_2(\eta^3-C_3H_5)$, where the addition of CO leads to the detection of $Ir(CO)_2(PPh_3)(\eta^3-C_3H_5)$, $Ir(CO)_3(PPh_3)(\eta^1-$ CH₂CH=CH₂), Ir(CO)₂(PPh₃)₂(COCH₂CH=CH₂) and Ir(CO)₃-(PPh₃)(COCH₂=CHCH₂).⁴²

These data do, however, confirm that under an atmosphere of CO, replacement of the phosphine by CO is possible. This observation indicates that phosphine-modified cobalt catalysts will produce unmodified species upon reaction with CO. Ligand exchange between CO and phosphite or phosphines in such allyl systems has previously been reported.43 In order to compare the ability of these systems to undergo phosphine replacement by CO a number of samples were prepared which contained a mixture of two of the complexes and 3 atm of CO at 295 K. Integration of the corresponding ³¹P signals enabled the relative stability of the complexes to phosphine loss to be assessed. For 1 (PPh₂Me) and 4 (PCy₃) the corresponding ratio proved to be 4.03:1 while for 1 and 3 it increased to 8.33:1, and for 1 and 5 it was 10.53:1. The PMe₂Ph system, 2, (PMe₂Ph) proved to be stable to phosphine loss at 295 K and 3 atm CO. It can therefore be concluded that the relative ability of $Co(\eta^3-C_3H_5)(CO)_2(PR_2R')$ to lose phosphine follows the trend $PMe_2Ph < PPh_2Me < PCy_3 < P(CH_2Ph)_3 <$ PPh3. These changes occur very slowly and were monitored over one week.

Reactivity of complexes 1-7 towards CO and H₂

When a toluene-d₈ solution of **1** was placed under 3 atm of a 2:1 mixture of CO and H₂ no reaction was evident at 313 K. Upon warming to 373 K, the corresponding ¹H NMR spectrum showed much weaker *p*-H₂ enhanced signals for propene and propane than when such a sample was under 3 atm of *p*-H₂ alone and at 313 K. In addition, five new *p*-H₂ enhanced signals were also detected in clear regions of the spectrum at δ 3.40, δ 3.10, δ 1.61, δ 1.13, δ 0.86, δ 0.80 and δ 0.72 (Fig. 3). The corresponding COSY spectrum connected the δ 3.38 signal (t, *J*_{HH} = 7 Hz) to those at δ 1.61 (sextet, *J*_{HH} = 7 Hz) and δ 1.13 (t, *J*_{HH} = 7 Hz), confirming that a linear CH₂CH₂CH₃ group has been formed with protons

from p-H₂ being placed on all three of the carbon centres. This spectrum also confirmed that the additional ¹H signal at δ 3.40 (septet, $J_{\rm HH} = 8$ Hz) coupled to a signal at δ 1.13 (d, $J_{\rm HH} = 8$ Hz) which indicated that a species containing a CH(CH₃)₂ group was also formed.



Fig. 3 ¹H spectrum of a toluene- d_8 solution of **1** at 373 K in the presence of a mixture of H_2 and CO.

When this reaction was repeated with ¹³CO, both of the terminal alkyl proton signals showed additional ¹³C splittings that arose

 Table 6
 Selected NMR data for the acyl complexes 1a–7a and 1b–7b

from ¹³C signals that appeared at δ 234.5 and δ 239.8 respectively. Since both the latter resonances exhibited doublet multiplicities due to ³¹P–¹³C couplings ($J_{PC} = 51$ and 44 Hz respectively), their origin as metal acyl groups, *trans* to a single phosphine ligand, was confirmed. The corresponding complexes are therefore the linear acyl containing species Co(COCH₂CH₂CH₃)(CO)₃(PPh₂Me) (**1a**) and the branched complex Co(COCH(CH₃)₂)(CO)₃(PPh₂Me) (**1b**) with structures shown in Scheme 4. In view of the fact that **1a** and **1b** contain PPh₂Me, it is possible to conclude that **1** reacts initially with H₂ *via* CO loss and that Co(η^3 -C₃H₅)(CO)(PR₂R')(H)₂ does indeed correspond to the initially formed dihydride complex as suggested earlier. NMR data for these species can be found in Table 6.



Scheme 4 Structural representation of $Co(COCH_2CH_2CH_3)(CO)_3$ -(PPh₂Me) (1a) and the branched complex $Co(COCH(CH_3)_2)(CO)_3$ -(PPh₂Me) (1b) detected when a toluene solution of 1 is warmed with CO and *p*-H₂.

		$\begin{array}{c} H_2^{b}C \\ \downarrow \\ O \\ OC \\ OC'' \\ OC'' \\ PR_2R' \end{array} $	OC OC OC PR	CH ₃ - H—CH ₃ -CO 2 ^{R'}	
		1a - 7a	1b	- 7b	
	Linear acyls (a) Co(COCH ₂ CH ₂ CH	$H_3)(CO)_3(PR_2R')$		Branched acyls (b) Co(COCH(CH ₃) ₂)(CO) ₃ (PR ₂ R')	
Precursor	¹ H	$^{13}\mathrm{CO}_{acyl}$	$^{31}P\{^{1}H\}$	¹ H	$^{13}CO_{acyl}$
1	3.10 (t), $CH_{2^{a}}$, $J_{HH} = 7 Hz$ 1.61 (sextet), $CH_{2^{b}}$, $J_{HH} = 7 Hz$ 0.87 (t), CH_{3} , $J_{HH} = 7 Hz$	234.5 (d), $J_{\rm PC} = 51$ Hz	32.4 (s)	3.40 (septet), CH, $J_{\rm HH} = 7$ Hz 1.14 (d), $J_{\rm HH} = 7$ Hz	239.8 (d), <i>J</i> _{PC} = 44 Hz
2	3.06 (t), CH_2^a , $J_{HH} = 7 Hz$ 1.60 (sextet), CH_2^b , $J_{HH} = 7 Hz$ 0.86 (t), CH_3 , $J_{HH} = 7 Hz$	_	—	3.34 (septet), CH, $J_{\rm HH} = 7$ Hz 1.13 (d), $J_{\rm HH} = 7$ Hz	_
3	2.99 (t), $CH_{2^{a}}$, $J_{HH} = 7 Hz$ 1.56 (sextet), $CH_{2^{b}}$, $J_{HH} = 7 Hz$ 0.83 (t), CH_{3} , $J_{HH} = 7 Hz$	234.8 (d), $J_{\rm PC} = 45$ Hz	50.5 (s)	3.27 (septet), CH, $J_{\rm HH} = 7$ Hz 1.07 (d), $J_{\rm HH} = 7$ Hz	239.9 (d), $J_{\rm PC} = 43$ Hz
4	3.22 (t), CH_2^{a} , $J_{HH} = 7 Hz$ 1.67 (sextet), CH_2^{b} , $J_{HH} = 7 Hz$ 0.92 (t), CH_3 , $J_{HH} = 7 Hz$	235.6 (d), $J_{\rm PC} = 39 {\rm Hz}$	62.0 (s)	3.37 (septet), CH, $J_{\rm HH} = 7$ Hz 1.20 (d), $J_{\rm HH} = 7$ Hz	240.9 (d), <i>J</i> _{PC} = 40.5 Hz
5	3.18 (t) CH_2^{a} , $J_{HH} = 7 Hz$ 1.64 (sextet), CH_2^{b} , $J_{HH} = 7 Hz$ 0.87 (t), CH_3 , $J_{HH} = 7 Hz$	234.1 (d), $J_{\rm PC} = 57$ Hz	50.1 (s)	3.50 (septet), CH, $J_{\rm HH} = 7$ Hz 1.17 (d), $J_{\rm HH} = 7$ Hz	239.4 (d), $J_{\rm PC} = 46$ Hz
6	3.07 (t), $CH_{2^{a}}$, $J_{HH} = 6.5 Hz$ 1.58 (sextet), $CH_{2^{b}}$, $J_{HH} = 7 Hz$ 0.82 (t), CH_{3} , $J_{HH} = 7 Hz$	234.1 (d), $J_{\rm PC} = 41$ Hz	_	3.57 (septet), CH, $J_{\rm HH} = 7$ Hz 1.08 (d), $J_{\rm HH} = 7$ Hz	239.2 (d), $J_{\rm PC} = 34$ Hz
7	3.13 (t), CH_2^{a} , $J_{HH} = 6 Hz$ 1.61 (sextet), CH_2^{b} , $J_{HH} = 6.5 Hz$ 0.85 (t), CH_3 , $J_{HH} = 7 Hz$	234.05 (d), $J_{\rm PC} = 35 \rm Hz$	_	3.43 (septet), CH, $J_{\rm HH} = 6.5$ Hz 1.135 (d), $J_{\rm HH} = 7$ Hz	239.0 (d) $J_{\rm PC} = 41 \text{ Hz}$

The original studies by Heck and Breslow led to an accepted mechanism for hydroformylation involving a mono-hydride precursor which binds the alkene prior to forming a metal alkyl which goes on to form a metal acyl complex that eliminates the aldehyde after H₂ addition.³ We have already described in this manuscript how 1 reacts with $p-H_2$ to form propene via a metal-propene-hydride. The observation of 1a and 1b as p-H₂ enhanced products can therefore be accounted for by the trapping of the corresponding 16-electron intermediates, Co(CO)₂(PR₂R')(C(O)CH₂CH₂CH₃) and Co(CO)₂(PR₂R') $(COCH(CH_3)_2)$ with CO rather than H₂. This information is summarised in Scheme 5. The protons that are incorporated in these products from a single p-H₂ molecule are shown in red. These protons move around the indicated molecular framework according to the processes illustrated in Scheme 5. We note that the enhanced signals seen in the NMR spectra for molecules possessing the linear site B arrangement in product 1a can be produced directly from the allyl dihydride complex while molecules corresponding to the arrangement necessary for linear site A in 1a arise via a re-linearised branched intermediate; this intermediate reacts competitively with this process to form 1b.



Scheme 5 Transformations accounting for the p-H₂ enhanced NMR signals seen at sites where the protons appear in red.

In these ¹H NMR spectra, p-H₂ enhanced resonances are also visible at δ 0.82 and δ 0.72 for the free aldehydes CH(O)CH(CH₃)₂ and CH(O)CH₂CH₂CH₃ respectively. The room temperature proton resonance positions for the linear aldehyde CH(O)CH₂CH₂CH₃ proved to be δ 0.7 (t, $J_{\text{HH}} = 7$ Hz), δ 1.31 (m), δ 1.76 (dt, $J_{\text{HH}} = 2$ and 7 Hz), δ 9.29 (t, 2 Hz) while those for the branched aldehyde CH(O)CH(CH₃)₂ appeared at 0.77 (d, $J_{\text{HH}} = 7$ Hz), δ 1.62 (m) and δ 9.24 (d, 1 Hz).

When the ¹H NMR spectra on this sample were recorded at 373 K, additional weak para-hydrogen enhanced signals were seen at δ 4.17 (dd, $J_{\rm HH}$ = 8 and 4 Hz, 3.99 (d, $J_{\rm HH}$ = 6 Hz), 3.92 (dd, $J_{\rm HH} = 7$ and 6 Hz), and 3.73 (d, $J_{\rm HH} = 6$ Hz) (Fig. 4). These peaks all appear with antiphase character, and occur in a region that is characteristic of metal-alkene 1H NMR signals.44 When a COSY spectrum was recorded, the strongest of these peaks, resonating at δ 4.17, proved to be coupled to three other resonances at δ 1.85, 1.65 and 1.011. Examination of the multiplicity of these resonances confirmed that the unique proton yielding the peak at $\delta 4.17$ is α to the methyl of the bound propene which resonates at δ 1.011, while the peaks at δ 1.85 and 1.65 correspond to protons that are *trans* and cis to this group respectively. This information conclusively demonstrates that a coupled set of resonances corresponding to a bound propene ligand has been observed. Additional correlations were visible in such spectra between the ¹H resonance at δ 3.92 and a new peak at δ 1.68, and between the ¹H resonance at δ 3.99 and a new peak at δ 1.82. The signal to noise ratio for these signals, however, proved to be insufficient to locate the additional resonances necessary for the full characterization of the propene ligands.



Fig. 4 Additional signals observed in the ¹H NMR spectrum of 1 in the presence of H_2 and CO at 373 K.

The peaks at δ 3.92 (dd, $J_{\rm HH}$ = 7 and 6 Hz) and 3.73 (d, $J_{\rm HH}$ = 6 Hz) showed a similar dramatic increase in size on warming to 383 K, while the two peaks at δ 4.17 and δ 3.99 decreased in intensity by a similar amount. These peaks therefore appear to belong to four distinct propene complexes. Unfortunately, when samples containing ¹³CO labelled materials were employed, none of these proton signals proved to connect to either a CoCOR resonance or a CoCO resonance in the corresponding ¹H-¹³C HMQC experiment. Nonetheless, we suggest that the trapping of the 16-electron fragments Co(COCH₂CH₂CH₃)(CO)₂(PPh₂Me) and Co(COCH(CH₃)₂)(CO)₂(PPh₂Me) required to form 1a and 1b, by (PHIP enhanced) propene rather than CO accounts for the observation of these species. The signals therefore most likely arise from isomers of Co(COCH₂CH₂CH₃)(CO)₂(PPh₂Me)(propene) and $Co(COCH(CH_3)_2)(CO)_2(PPh_2Me)(propene)$ such as those shown in Scheme 6 which might be differentiated by the relative orientation of the alkene.

When the reactions of the corresponding complexes 2-7 with $p-H_2$ and CO are observed by NMR spectroscopy the analogous



Scheme 6 Additional species detected during reaction of 1 with $p-H_2$ and CO at 373 K: Co(COCH₂CH₂CH₃)(CO)₂(PPh₂Me)(propene) and Co(COCH(CH₃)₂)(CO)₂(PPh₂Me)(propene). Only one isomer of each is illustrated.

products to **1a** and **1b** were observed in each case. The NMR characteristics of these materials are listed in Table 6. Resonances of the type indicated for bound propene ligands were only visible in NMR spectra obtained for samples of **1**, **2** and **6**. It should further be noted that when samples of **5** were cooled back to room temperature at the end of the experiments, crystals of $[Co(CO)_3PPh_3]_2$ consistently precipitated from solution. The structure of $[Co(CO)_3PPh_3]_2$ is illustrated in Fig. 5, and appropriate X-ray data listed in Table 7. Complexes of this type have been proposed to react with H₂ to form the active precatalyst HCo(CO)₃(PR₃) necessary for modified cobalt based hydroformylation catalysis.⁴⁵

Table 7 Selected bond lengths (Å) and angles (°) for [Co(CO)₃PPh₃]₂

Assignment	Value
$Co(1)-Co(1)#1^{a}$	2.6506(9)
Co(1) - P(1)	2.1895(9)
Co(1-C(1))	1.7845(16)
C(1) - O(1)	1.1467(19)
C(1) - Co(1) - P(1)	94.25(5)
O(1) - C(1) - Co(1)	178.83(13)
$C(1) - Co(1) - C(1) \# 2^{b}$	119.457(12)

^{*a*}#1 = inversion centred on midpoint of Co–Co bond (11/3 - x, 2/3 - y, 2/3 - z). ^{*b*}#2 = 3-fold rotation about Co–Co axis, (1 - y, x - y, z).



Fig. 5 ORTEP diagram of $[Co(CO)_3PPh_3]_2$. Ellipsoids drawn at 50% probability level. The asymmetric unit corresponded to 1/6th of the molecule as labelled. The $R\bar{3}$ space-group defines the rest of the molecule (inversion centre located at the midpoint of the Co–Co bond and 3-fold rotation about the Co–Co axis).

Reactivity of 1 towards H₂ and d₁₀-diphenylacetylene

In this experiment, we aimed to form relatively high concentrations of p-H₂ enhanced cis-stilbene which might in turn replace the propene ligand in the previously proposed species Co(CO)(PPh₂Me)(H)(propene). This approach has been used previously to detect a palladium alkyl cation during studies involving diphenylacetylene and para-hydrogen.^{22,46} An NMR sample was therefore prepared that contained a 100-fold excess of d_{10} -diphenylacetylene relative to 1, and the reaction with p-H₂ examined at 313 K. d₁₀-PhC≡CPh was indeed hydrogenated under these reaction conditions, and the formation of para-hydrogen enhanced cis-stilbene indicated by the observation of an emission signal at δ 6.47. In addition, new *para*-hydrogen enhanced proton signals were observed at δ 3.51, δ 3.33 and δ 3.30. These three resonances proved to be coupled in a COSY experiment, and they all showed a further ³¹P splitting. A ¹H-³¹P-HMQC data set located the phosphorus resonance causing these splittings at δ 39.1. When mono-¹³C labelled d₁₀-diphenylacetylene, d₁₀-PhC≡¹³CPh was utilized, the first two proton resonances coupled to a single 13 C NMR signal at δ 40.02, which appeared as a broad singlet. The third ¹H NMR signal which resonates at δ 3.30 coupled to a second ¹³C resonance, now at δ 48.5, which appears as a phosphorus coupled doublet where $J_{PC} = 19$ Hz. The formation of an alkyl group bound directly to cobalt is therefore indicated. When the same reaction was examined with a cobalt precursor labelled with ¹³CO, no additional splittings were seen in any of these parahydrogen enhanced signals, and the terminal CH₂ group failed to couple to an acyl¹³C signal, as would have been expected if this was a CO insertion product such as those described earlier in this paper. These results therefore suggest that the large excess of d₁₀-diphenylacetylene facilitates the formation of *cis*-stilbene which is trapped by the CoH(CO)₂(PPh₂Me) intermediate liberated by the formation of propane. The product that is detected therefore corresponds to Co(CO)₃(PPh₂Me)(CHPhCH₂Ph) (Scheme 7).



Scheme 7 Additional species detected during the reaction of 1 with p-H₂ and d₁₀-diphenylacetylene at 313 K.

Under these conditions we also see a new p-H₂ enhanced peak at δ 0.84 which couples to two other protons and appears with a chemical shift which is very close to that of the methyl resonance of free propane. In the COSY spectrum this peak proved to couple to additional resonances at δ 1.59 and δ 3.09. Of these two signals, the former resonance is *para*-hydrogen enhanced, and the peak multiplicities of the PHIP enhanced signals indicate the presence of couplings to 2 protons and 5 protons respectively. Since the δ 3.09 resonance does not appear in the one dimensional ¹H NMR spectrum it can be concluded that the associated protons located in this site do not arise from *para*-hydrogen. These data confirm however the formation of a linear alkyl group, with the lower temperatures used here facilitating its detection. The chemical shift of the CH₂ moiety at δ 3.09 however suggests the trapping of Co(CO)₂(PPh₂Me)(COCH₂CH₂CH₃) by PhC=CPh, the ligand in solution that has the highest concentration, and hence the detection of Co(CO)₂(PPh₂Me)(COCH₂CH₂CH₃)(PhC=CPh).

In view of the high cost of the ¹³C labelled d₁₀-diphenylacetylene, when this experiment was repeated with the labelled precursor, only a 10-fold excess of the substrate relative to metal was used. The ¹H NMR resonance at δ 3.09 now proved to be enhanced in accordance with more extensive hydrogen scrambling. This suggests that when a large excess of substrate is employed, the ability of the system to undergo the necessary proton exchange to see enhancement is substantially reduced.

When a sample of **1** was shaken with CO, H_2 and d_{10} -diphenylacetylene, these extra p- H_2 enhanced species are produced in much smaller amounts than when p- H_2 and d_{10} -diphenylacetylene alone are employed. The reaction with CO therefore now competes effectively with hydrogenation and reduces the amounts of these species. As a consequence, we were unable to obtain more definitive data and thereby confirm their identity.

Catalytic studies on the reactivity of complexes 1–8 towards CO and $H_{\rm 2}$

In order to compare the reactivity of these systems under hydroformylation conditions, we have undertaken a number of studies using constant concentrations of the catalyst precursor and a $CO: H_2$ ratio of 2:1.

For the PCy₃ precursor, **4**, the relative size of the observed ¹H NMR signals due to the aldehydes, propene and propane, relative to those of the solvent, consistently increased with an increase in temperature. There was, however, an increased preference for the formation of the linear aldehyde at higher temperatures. Fig. 6 summarizes these variations. The two distinct points of reference



Fig. 6 Plot of the p-H₂ based NMR signal intensities for species 4a, 4b and the corresponding aldehydes as a function of temperature for samples of 1 reacting in toluene with 3 atm of a 2:1 mixture of CO and H₂ normalised relative to free branched aldehyde. (Note, linear aldehyde (n) (**m**) and branched aldehyde (**m**) data obtained from ¹H signals measured using normal methods when the thermally polarized states are visible).

shown for the linear acyl containing species 4a [(\square) and (\square)] refer to signals obtained from the p-H₂ enhanced proton NMR resonances at the COCH₂ site and the terminal methyl site respectively; the resonance for the connecting CH₂ site appeared in a congested region of the spectrum and could only be located by COSY spectroscopy. The terminal methyl resonance seen for the branched acyl containing species 4b was used to obtain the data represented by the (=) label. para-Hydrogen enhanced signals were also used to probe the branched to linear (**•**) free aldehyde composition at very early stages in the reaction. In order to establish that the p-H₂ based signal strength trends are meaningful, we also measured the linear/branched aldehyde ratio at the end of the experiment when the associated signals arise from "normal" magnetisation. These data are indicated with the () label. It can be seen that the ratio of free linear to branched aldehyde follows the same trend as that obtained from p-H₂ enhanced signals that are seen at early stages in the reaction. This validates the approach and suggests meaningful trends might be observed when the intensities of $p-H_2$ enhanced signals are compared.

The relative signal strengths for the COCH₂ group (\blacksquare) and the terminal methyl group (\blacksquare) of **4a** become equal at temperatures greater than 377 K. This suggests that the *p*-H₂ label is now randomly distributed within the corresponding acyl group and hence indicates that the proton exchange pathways shown in Scheme 5 should be facile.

Roe has used high pressure NMR methods to demonstrate that the thermal loss of CO from CH₃C(O)Co(CO)₄ occurs at a rate of 11.5 s⁻¹ at 353 K.⁸ This rate would be sufficient to see magnetisation transfer from such a species into the free aldehyde by NMR spectroscopy. A series of 1D EXSY experiments were therefore undertaken to test for magnetization transfer from **4a** and **4b** into the corresponding aldehydes. None was observed. This result indicates that the electron donating properties of the phosphine dramatically stabilise **4a** with respect to CO loss when compared to the unmodified form. Furthermore, it confirms that the enhanced NMR signals seen for the free aldehydes arise from the trapping of the corresponding 16-electron intermediates Co(COCH₂CH₂CH₃)(CO)₂(PCy₃) and Co(COCH(CH₃)₂)(CO)₂(PCy₃) with H₂ (which leads to rapid aldehyde elimination) rather than CO (which leads to **4a** or **4b**).

The variation in the observed aldehyde product ratios illustrated in Fig. 6 therefore reflects higher turnovers for the linear product at higher reaction temperatures. Logically, this effect might correspond to a depletion in the amount of 4a that is detected which in turn will reduce the observed ratio of 4a : 4b. This effect is supported by the data presented in both Fig. 6 and 7 where the final aldehyde ratios are plotted as a function of temperature with the PCy₃ data appearing as a and showing an increase with temperature as predicted.

Fig. 7 also demonstrates that the PMe₂Ph and PPh₂Me ligand systems show a similar increase in selectivity for the linear product with increase in reaction temperature. In contrast, however, the PPh₃, dppe and dppm systems show a fall in selectivity over the same temperature range. This situation is complicated for the activating P(Ch₂Ph)₃ phosphine where the selectivity initially falls and then increases with temperature. This observation actually reflects the fact that the P(Ch₂Ph)₃ system produces secondary oligomerization products at higher temperatures and consequently the full product distribution is not accounted for in this plot.⁴⁷



Fig. 7 Final free linear/branched aldehyde product ratios observed as a function of temperature and phosphine for an initial 2:1 ratio of CO to H₂. Phosphines identified in key.

Nonetheless, it is clear that the phosphine plays a role in controlling this reaction selectively.

Fig. 8 shows how the ratio of the PHIP enhanced signals for the linear to branched intermediates (**a**) and (**b**) vary with temperature. Overall, the highest selectivity for the linear product $Co(COCH_2CH_2CH_3)(CO)_2(PR_3)$ is found with PCy₃ as might be expected for the largest phosphine. These data also reveal that the linear CO addition products, $Co(COCH_2CH_2CH_3)(CO)_2(PR_2R')$, are not always favoured.



Fig. 8 Ratios of the observed PHIP enhanced ¹H NMR signals for linear cobalt product (a) to branched cobalt product (b) as a function of temperature for an initial 2:1 ratio of CO to H_2 .

In addition, these data reveal for the PMe₂Ph and PPh₂Me systems that the ratio of the corresponding linear and branched intermediates hardly changes over the temperature range 368–393 K. In contrast, there is a much higher change in the free aldehyde product ratio. These data must therefore mask a further trend. This process is revealed in Fig. 9, which shows how the ratio of the normalised signal strengths for the intensities of site B (the CH₃ group) and site A (the COCH₂ group as indicated in Scheme 5) of the linear species Co(COCH₂CH₂CH₃)(CO)₂(PR₂R') vary with phosphine. This plot therefore provides an insight into both the selectivity of the hydride transfer step and its reversibility. For example if a random arrangement of the *p*-H₂ label were to result the ratio would be of 1:1. As the temperature increases, it might be expected that the reversible proton transfers of Scheme 5 get faster and hence the observed ratio tends to 1:1. This trend is most



Fig. 9 Ratio of the normalised ¹H signal intensities for linear site B to linear site A in complexes 1a-7a as a function of temperature and phosphine for a CO: H₂ ratio of 2:1.

clearly seen in the case of the dppm system where the ratio starts off at 1.7:1 and falls towards 1:1 with increase in temperature. Consequently, there is therefore an increase in hydride transfer into the branched site with increase in temperature which corresponds with the fall in reaction selectivity seen for this phosphine. For the PCy₃ system, however, the initial ratio is less than one, and tends towards this value as the temperature is raised. This suggests that the propensity for hydride transfer into the terminal site increases with temperature and matches the trend for increased selectivity for linear aldehyde with increase in temperature.

For the other phosphines, there is a slight increase in this ratio with temperature. This suggests that there is essentially a random distribution of the *para*-hydrogen label to start and hence the ratio of the corresponding linear and branched intermediates is initially under thermodynamic control. The reactions observed selectivity should therefore reflect directly the ratio of these species in solution rather than the rate constants for hydride ligand transfer to propene as suggested for the dppm system. When the ratio increases with temperature, it would therefore appear that CO insertion now competes more effectively with hydrogen label scrambling.

In order to explore how the relative ratios of H_2 and CO affect these reactions, we recorded a number of experiments at 373 K for the different precursors where the total pressure was maintained at 3 atm, but the CO to H_2 ratio was changed from 4:1, through 1:1 and 2:1 to 3:1. Fig. 10 shows the results of this process and reveals that the reaction final product distribution shows a



Fig. 10 Effect of the $CO:H_2$ ratio on the free aldehyde product distribution as a function of phosphine for a series of reactions that were completed at 373 K.

complex dependence on the CO to H_2 ratio. The 1:2 ratio shows the highest selectivity for the formation of linear aldehyde in the case of both the PCy₃ and PPh₃ based systems. In contrast, both the PMe₂Ph and PPh₂Me systems show a mutually similar trend where the selectivity rises with CO composition. The dppe and dppm systems also result in higher selectivity for linear aldehyde at higher CO ratios, but their reactions are far more sensitive to this change than either the PMe₂Ph or PPh₂Me systems. We cannot however exclude potential variations in the contributions from chelated and non-chelated species.

Conclusions

The syntheses of $Co(\eta^3-C_3H_5)(CO)_2PR_2R'$ (R, R' = Ph, Me; R, R' = Me, Ph; R = R' = Ph, Cy, CH₂Ph) and $Co(\eta^3-C_3H_5)(CO)(L)$ (L = dmpe and dppe) are described, and X-ray structures for $Co(\eta^3-C_3H_5)(CO)(dppe)$ and the PPh₂Me, PCy₃ derivatives reported. The relative ability of $Co(\eta^3-C_3H_5)(CO)_2(PR_2R')$ to exchange phosphine for CO follows the trend PMe₂Ph < PPh₂Me < PCy₃ < P(CH₂Ph)₃ < PPh₃. According to Tolman,³⁰ the basicity of these ligands follows the order PCy₃ > PMe₂Ph > P(CH₂Ph)₃ > PPh₂Me > PPh₃ while their steric effect increases according to PMe₂Ph < PPh₂Me < PPh₃ < P(CH₂Ph)₃ < PCy₃. Consequently we can deduce that the ability of **1–6** to undergo phosphine exchange is highly influenced by the steric effect of the phosphine.

Reactions of these allyl complexes with *para*-hydrogen (*p*-H₂) lead to the observation of *para*-hydrogen induced polarisation in both liberated propene and propane. The temperature at which these products are first seen varies with the phosphine according to the listing PPh₂Me < PMe₂Ph < dppm < dppe ~ P(CH₂Ph)₃ < PPh₃ < PCy₃. These reactions proceed as a consequence of CO loss. Consequently, the better the electron donating properties of the phosphine, the stronger the CoCO bond; this accounts for the higher activation temperatures of the PCy₃ system, but given the fact PPh₃ containing system also requires a high temperature steric effects must also play their role on this reaction.

The reaction of the allyl complexes with both CO and H₂ leads to the detection of linear acyl containing species Co(COCH₂CH₂CH₃)(CO)₃(PR₂R') and branched acyl complexes $Co(COCH(CH_3)_2)(CO)_3(PR_2R')$ via the PHIP effect. In the case of PPh₂Me, additional signals that have been attributed to Co(COCH₂CH₂CH₃)(CO)₂(PPh₂Me)(propene) and $Co(COCH(CH_3)_2)(CO)_2(PPh_2Me)$ (propene). Similar signals were also seen during studies on the PMe₂Ph and dppm systems. This information suggests that when the phosphine is electron rich, and relatively small, the liberated propene can bind sufficiently well as to allow the detection of these species. Furthermore, when the reactions of H_2 and diphenylacetylene are studied with the PPh₂Me based precursor, the detection of Co(CO)₃(PPh₂Me)(CHPhCH₂Ph) rather than its acyl form is achieved. This must reflect the stronger M-CHPh- bond strength when compared to M–CH₂- which acts to reduce the rate of acyl intermediate formation.

Studies on how the appearance, and ratio, of the PHIP enhanced signals seen in these reaction vary as a function of reaction temperature and H₂ to CO ratio have also been described. These data revealed that the PMe₂Ph and PPh₂Me based systems yield the highest selectivity for the linear hydroformylation products. The PHIP enhanced signal profiles also provide information

about how the relative rates of key steps leading to linear and branched hydroformylation products compete for the different phosphines. While the PPh₂Me system yields one of the largest differences in the ratio of the signal strengths seen for the aldehyde products, the corresponding difference in signal ratios for the intermediates Co(COCH₂CH₂CH₃)(CO)₃(PPh₂Me) and Co(COCH(CH₃)₂)(CO)₃(PPh₂Me) is close to one. This suggests that there is less of the Co(COCH₂CH₂CH₃)(CO)₃(PPh₂Me) form present because more of it is converted into the aldehyde via H₂ addition to Co(COCH₂CH₂CH₃)(CO)₂(PPh₂Me) rather than CO coordination. Furthermore, the ratio of the signal intensities of the linear site B to that of A for PPh₂Me is always greater than one and increases with increasing temperature. These data therefore reveal that the degree of alkyl/alkenehydride interconversion falls with increase in temperatures and hence confirm that productive aldehyde formation competes with alkyl group isomerisation.

Consequently it can be seen that at low temperatures, the reaction selectivity is best viewed on the basis of the initial kinetic preference for hydride insertion to form a branched intermediate over that which leads to the linear analogue for dppm. At higher temperatures, there is a rapid equilibration between these intermediates as evidenced by the fact that the *para*-hydrogen label is randomly arranged between sites A and B. This suggests that their ratio reaches a level which is controlled by their thermodynamic stability. The ensuing reactions selectivity must then reflect the relative rates of H₂ addition to the corresponding 16-electron intermediates.

Acknowledgements

SBD and CG are grateful to Sasol Technology UK Ltd. for support. The EPSRC is acknowledged for providing funding for the diffractometer.

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