Rhodium(I) complexes containing the enolate of *N*-acetyl-3-butanoyltetramic acid (Habta) and the crystal structure of [Rh(abta){P(OPh)$_3$}$_2$]

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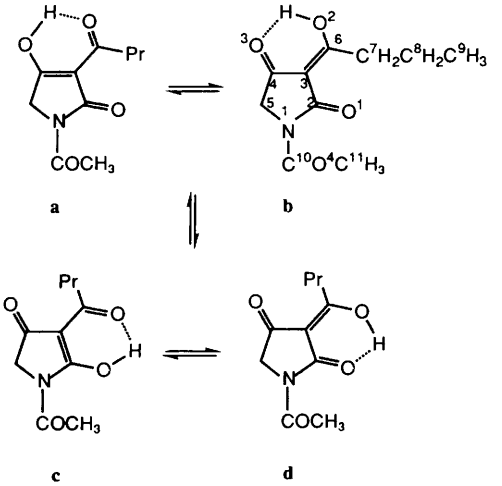
Reaction of *N*-acetyl-3-butanoyltetramic acid (Habta) (*N*-acetyl-3-butanoyl-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one) with [Rh(acac)(CO)$_2$] (acac = acetylacetonate) in a 1 : 1 ratio gave [Rh(abta)(CO)$_2$] **1** which underwent displacement of CO by either P(OPh)$_3$ or PPh$_3$ to give [Rh(abta)(CO)L] [L = P(OPh)$_3$ or **2** PPh$_3$ **4**] and [Rh(abta){P(OPh)$_3$}$_2$] **3**; the reaction of **4** with PPh$_3$ gave the five-co-ordinate complex [Rh(abta)(CO)(PPh$_3$)$_2$] **5**. The solid-state structure of **3** has been determined by X-ray diffraction. It shows that rhodium adopts a slightly distorted square-planar geometry with the abta enolate ligand adopting an *O,O'* mode of co-ordination *via* the functionalities associated with C^4 and the acyl group at C^3 in the pyrrolidine ring. Under ^{13}CO, **3** is in equilibrium with **2** and **1** as shown by ^{13}C NMR spectroscopy. No evidence has been found for the formation of five-co-ordinate complexes through the addition of P(OPh)$_3$ to **2**.

The rhodium(I) complexes [Rh(acac){P(OPh)$_3$}$_2$] and [Rh(acac)(CO)(PPh$_3$)] (acac = acetylacetonate) in the presence of triphenyl-phosphite or -phosphine respectively are catalyst precursors for the hydroformylation of olefins under mild conditions [40 °C, 1 atm (*ca.* 10^5 Pa)].[1] Exchange of co-ordinated P(OPh)$_3$ or PPh$_3$ in these complexes with free phosphine has been studied by NMR spectroscopy but the stability of the complexes with four- *versus* five-co-ordination remains an open question.[2,3] The substitution of acac by other chelating monoanions has been less well studied for rhodium complexes and we are interested in understanding the mode of co-ordination of the enolate of *N*-acetyl-3-butanoyltetramic acid (*N*-acetyl-3-butanoyl-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one, Habta) which has the potential to co-ordinate in a variety of modes including that of a β-diketonate (see below).

This compound belongs to a family of tetramic acid derivatives which represent a growing class of natural products; they are pyrrolidine-2,4-diones acylated at the 3 position and exhibit a wide range of biological activity.[4] In solution, 3-acyltetramic acids exist as pairs of 'internal' (**a** ⇌ **b**, **c** ⇌ **d**) and 'external' (**ab** ⇌ **cd**) tautomers (Scheme 1).[5] Nuclear magnetic resonance measurements show that the interconversion between the external enolic tautomers (**ab** ⇌ **cd**) is comparatively slow on the NMR time-scale whereas there is fast interconversion between the pairs of internal tautomers **a** ⇌ **b** and **c** ⇌ **d**. Recently, it has been shown by X-ray diffraction that *N*-acetyl-3-butanoyltetramic acid adopts the tautomeric form **a** (Scheme 1) in the solid state.[6] Thus, there are many possible modes of co-ordination possible for Habta and abta to metals; these could involve mono- or bi-dentate co-ordination *via* nitrogen and/or oxygen. Although the biological activity of tetramic acid derivatives is claimed to be related to their complexing ability,[7] little is presently known about the structure of their metal complexes.[8,9]

This paper reports the preparation of rhodium(I) complexes containing abta together with their structural characterisation through the X-ray analysis of [Rh(abta){P(OPh)$_3$}$_2$] and NMR and IR spectroscopic measurements in solution. We find



Scheme 1

that rhodium(I)–abta complexes undergo analogous reactions to those found for rhodium(I)–acac complexes except on phosphite exchange and on addition of triphenylphosphine.

Results and Discussion

The addition of 1 equivalent of Habta to a yellow-green solution of [Rh(acac)(CO)$_2$] in CH_2Cl_2 results in complete substitution of acac by abta with formation of [Rh(abta)(CO)$_2$] **1**. Monitoring this reaction by IR spectroscopy showed that the bands due to [Rh(acac)(CO)$_2$] at 2085 and 2014 cm^{-1} are replaced within 1 h by two equally intense bands at 2095 and 2027 cm^{-1} due to the formation of **1** (see Table 1). Like [Rh(acac)(CO)$_2$], **1** sublimes under vacuum and is dichroic changing between blood-red and light green. The ^{13}C NMR spectrum of **1** (Table 2) consists of two equally intense resonances due to rhodium carbonyls which are inequivalent as

Table 1 Infrared* data for analogous rhodium complexes containing either abta or acac

Complex	abta		acac
	ν(C⋯O) + ν(C⋯C)	ν(CO)	ν(CO)
1	1605	2095, 2027	2085, 2014
2	1608	2020	2011
3	1612	—	—
4	1607	1990	1977
5	1631	1960	—

* Recorded as solutions in CH_2Cl_2.

Table 2 Carbon-13 NMR [a] data for rhodium(I)–abta complexes

Complex	T/K	δ(CO) [b]	^2J(P–CO)/Hz
1		182.7 (75.7), 182.6 (74.2)	—
2a [c]	193	186.22 (78.1)	32.2
2b [c]	193	186.17 (76.5)	32.2
4a	233	189.1 (78.8)	24.5
4b	233	188.6 (78.1)	24.5
5	213	191.0 (77.3)	16.8

[a] Recorded as solutions in CH_2Cl_2. [b] Values of ^1J(Rh–CO)/Hz are shown in parentheses. [c] Recorded as solutions in CH_2Cl_2 under an atmosphere of ^{13}CO.

a result of the asymmetry of co-ordinated abta; spectroscopic data for all the abta complexes are consistent with its co-ordination in an *O,O′* mode through functionalities associated with C^4 and C^6 as found by X-ray crystallography (see below), *i.e.* Rh replaces H in isomers **a**,**b** shown in Scheme 1.

The reaction of [Rh(acac)(CO){P(OPh)$_3$}] with Habta in a 1 : 1 ratio in CH_2Cl_2 results in a change from light yellow to pale orange. Infrared spectroscopy shows that there is a fast substitution of acac with a shift of the CO stretching frequency from 2011 to 2020 cm^{-1} consistent with the formation of [Rh(abta)(CO){P(OPh)$_3$}] **2**. This complex could also be obtained by addition of a stoichiometric amount of triphenyl phosphite to a solution of the dicarbonyl complex **1**. Since abta is asymmetric, complex **2** can exist as two isomers **2a** and **2b** and two resonances of approximately equal intensity are observed for the P(OPh)$_3$ and CO groups in both the ^{31}P and ^{13}C NMR spectra, respectively. This suggests that the two co-ordinating oxygen atoms of abta exert a comparable *trans* influence leading to the formation of equal amounts of both isomers.

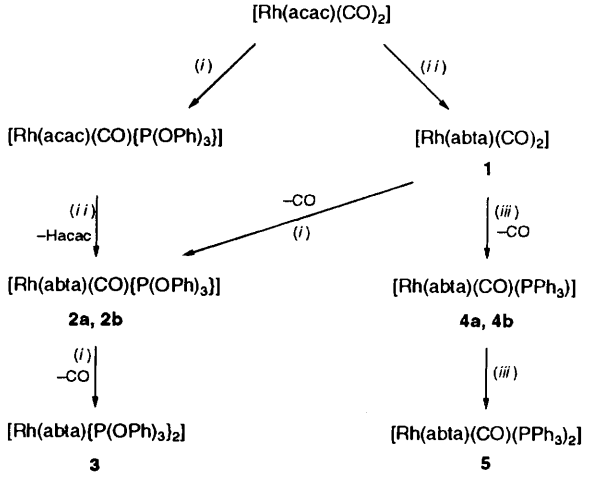
Similarly, addition of 1 equivalent of triphenyl phosphite to a solution of complex **2** results in the formation of [Rh(abta)-{P(OPh)$_3$}$_2$] **3** which, as expected, contained no peak in the CO stretching region of the IR spectrum and the ^{31}P NMR spectrum consists of an ABX spin system due to the asymmetry of abta; this is entirely in accord with the crystal structure (see below).

Addition of 1 equivalent of Habta to a light yellow solution of [Rh(acac)(CO)(PPh$_3$)] in CH_2Cl_2 results in a shift of the CO stretching vibration from 1990 to 1977 cm^{-1} consistent with the formation of [Rh(abta)(CO)(PPh$_3$)] **4**. The substitution reaction in this case is faster than that leading to the formation of **1**. It is also possible to prepare **4** by addition of a stoichiometric amount of PPh$_3$ to a solution of **1**, Scheme 2. As found for **2**, both ^{13}C and ^{31}P NMR data are consistent with the presence of two isomers due to **4a** and **4b** but in this case they are not equally intense (*ca.* 55 : 45) which enables the ^{13}C and ^{31}P data to be related to one isomer. In fact, the ^{13}C and ^{31}P resonances for **4a** both occur at lower field than those of **4b** but it is not possible to relate these NMR data to individual isomers. Nevertheless, the values of ^1J(Rh–P) for both isomers are *ca.* 175 Hz (Table 3). It is well known that ^1J(Rh–P) correlates well with *trans* influence,[10] with the value for a phosphine *trans* to an

Table 3 ^{31}P-{^1H} NMR [a] data for rhodium(I)–abta complexes

Complex	T/K	δ(P) [b]
2a	298	117.8 (296.5)
2b	298	117.5 (290.9)
3 [c]	298	122.0 (307.2), 122.3 (310.2)
4a	243	47.92 (174.5)
4b	243	47.89 (176.8)
5	213	34.3 (131.0)

[a] Recorded as solutions in CH_2Cl_2. [b] Values of ^1J(Rh–P) are shown in parentheses. [c] ^1J(Rh–P) and ^2J(P–P) 102.6 Hz determined by spectral simulation.



Scheme 2 (*i*) P(OPh)$_3$; (*ii*) Habta; (*iii*) PPh$_3$

oxygen in [Rh(RCOCHCOR′)(CO)(PPh$_3$)] being in the range 175–187 Hz,[11] whereas the corresponding value for nitrogen in the *trans* position is expected to be smaller. {J(Rh–P) for P *trans* to X in [RhX(PPh$_3$)$_3$]$^+$ is 168 Hz for X = NH_3 and 187 Hz for X = ONO_2^-.}[12] Thus, co-ordination through nitogen can be ruled out.

For complexes related to **2** and **4** containing unsymmetrically substituted β-diketonates only one isomer has been reported for [Rh(RCOCHCOR′)(CO){P(OPh)$_3$}] complexes and two isomers for [Rh(RCOCHCOR′)(CO)(PPh$_3$)].[11]

The monophosphine complex **4** reacts with 1 equivalent of triphenylphosphine in CH_2Cl_2 to give [Rh(abta)(CO)(PPh$_3$)$_2$] **5** [equation (1)], which could be isolated as yellow crystals.

$$[Rh(abta)(CO)(PPh_3)] + PPh_3 \longrightarrow [Rh(abta)(CO)(PPh_3)_2] \quad (1)$$

Five-co-ordinate β-diketonate complexes with two triphenyl-phosphine ligands such as **5** have not been isolated previously, although the acac analogue has been suggested as an intermediate in the PPh$_3$ exchange of [Rh(acac)(CO)(PPh$_3$)] in the presence of free PPh$_3$.[2]

The syntheses of the rhodium(I)–abta complexes **1**–**5** are summarised in Scheme 2 and substitution of acac by abta, as exemplified in equation (2), represents a mild and selective way

$$[Rh(acac)L_2] + Habta \longrightarrow [Rh(abta)L_2] + Hacac \quad (2)$$

to co-ordinate abta to rhodium, bearing in mind that many Rh–acac complexes are prepared with an excess of acetylacetone under reflux. These reactions add to the growing number of examples involving displacement of acac by a stronger acid. Previous examples include the functional phosphine Ph_2P-$CH_2C(O)Ph$ which substitutes acac in [Rh(acac)(CO)(PPh$_3$)] and [Ni(acac)$_2$] to give [Rh{$Ph_2PCH{=}C(=O)Ph$}(CO)-(PPh$_3$)] and [Ni{$Ph_2PCH{=}C(=O)Ph$}$_2$], respectively,[13,14]

displacement of acac from [Rh(acac)(dien)] (dien = diethylenetriamine) by pyrazole coordinated to platinum and from $[UO_2(acac)_2L]$ (L = dimethylformamide or trimethyl phosphate) by dibenzoylmethanate.[15,16]

The IR data for the abta compounds **1**–**5** and the analogous acac complexes are given in Table 1. All the CO stretching frequencies of the abta complexes are shifted to higher frequency (*ca.* 10 cm^{-1}) compared with their acac analogues. This is consistent with Habta having one more carbonyl group connected to the carbon bearing the acidic proton than Hacac making abta more electron-withdrawing than acac; this also makes Habta a stronger acid than Hacac. The fact that $[Rh(abta)(CO)(PPh_3)_2]$ **5** is formed can also be attributed to this difference between Habta and Hacac: unlike acac, the greater electron-withdrawing ability of abta stabilises complex **5** by accepting some of the additional electron density donated by the additional phosphine ligand.

As can be seen from the crystal structure of $[Rh(abta)\{P(OPh)_3\}_2]$ (see below), abta is co-ordinated in an *O*,*O*′-mode through the functionalities associated with C^4 and the acyl group at C^3 in the pyrrolidine ring. The IR and NMR data are consistent with this unique mode of co-ordination for all of the abta complexes. In the IR spectra for **1**–**5** there is always a strong absorption in the range 1605–1612 cm^{-1} which can be attributed to a combination of the ν(C⋯O) and ν(C⋯C) vibrations of co-ordinated abta.

The ^{13}C and ^{31}P NMR spectra of complex **5**, at 213 K in CH_2Cl_2, consist of only one resonance. The ^{13}C spectrum consists of a doublet of triplets due to ^1J(Rh–CO) and ^2J(P–CO) respectively (see Table 2) indicating equivalent phosphines. The equivalence of the phosphines could be attributed to fluxional behaviour which five-co-ordinate complexes usually exhibit but the values of both δ(^{31}P) and *J*(Rh–P) are indicative of mutually *trans* phosphines and therefore a trigonal-bipyramidal structure with *trans*-PPh_3 accomodates all the experimental data.

Ligand exchange

Most surprisingly, the room-temperature ^{31}P NMR spectrum of a solution of complex **3** containing 1 equivalent of triphenylphosphite in CH_2Cl_2 shows severe line broadening of the doublet due to **3** and the singlet of free triphenyl phosphite indicative of a fast exchange of phosphite. The halfwidths of the resonances due to **3** and $P(OPh)_3$ are 69.6 and 30.4 Hz respectively while the halfwidths for $[Rh(acac)\{P(OPh)_3\}_2]$ and $P(OPh)_3$, under the same conditions, are 4.5 and 11.3 Hz respectively. Phosphite exchange has not been observed previously for $[Rh(RCOCHCOR')\{P(OPh)_3\}_2]$ complexes not even at a 10:1 ratio of phosphite to complex.[3c,11]

The phosphine complex **4** undergoes exchange with free phosphine at a rate faster than the NMR time-scale giving rise to just one broad resonance in the ^{31}P NMR spectrum. In order to get a well resolved doublet the spectrum must be recorded at temperatures below −30 °C. Exchange of PPh_3 in the corresponding acac compound has been observed in the presence of free phosphine. Increasing the free phosphine concentration in this case resulted in acceleration of the exchange rate, but not in an increase of the co-ordination number at the Rh^I.[3] Solutions of pure **5** give just one broad resonance because the free PPh_3, produced by dissociation to **4**, results in phosphine exchange.

Under ^{13}CO, complex **3** is in equilibrium with **2** and **1** and triphenyl phosphite, equation (3). We could not observe any

$$\mathbf{1} + 2\,P(OPh)_3 \rightleftharpoons \mathbf{2} + CO + P(OPh)_3 \rightleftharpoons \mathbf{3} + 2\,CO \quad (3)$$

five-co-ordinate intermediates by NMR, spectroscopy. Interestingly, it has been proposed on the basis of IR and ^1H NMR evidence that the acac complexes analogous to **2** and **3** add CO to form $[Rh(acac)(CO)_x\{P(OPh)_3\}_{3-x}]$ (x = 1 or 2, respectively).[3]

Crystal structure of $[Rh(abta)\{P(OPh)_3\}_2]$ 3

A view of the molecular structure of one of the two molecules in the asymmetric unit is shown in Fig. 1. There are no significant differences between the two molecules in the asymmetric unit. Selected bond lengths and angles are listed in Table 4. The rhodium shows essentially square-planar co-ordination. The abta ligand is co-ordinated through the oxygen atoms O(2) and O(3) as a β-diketonate anion. The Rh–P bond *trans* to O(2) [Rh(1)–P(1) 2.146(3) Å] is slightly longer than that *trans* to O(3) [Rh(1)–P(2) 2.132(4) Å]. The Rh–O bond distances [2.088(7) and 2.061(8) Å] compare well with those found in $[Rh(acac)\{P(OPh)_3\}_2]$ [2.067(5), 2.061(5), 2.081(5) and 2.065(5) Å] and $[Rh(PhCOCHCOCF_3)\{P(OPh)_3\}_2]$ [2.067(6), 2.070(6)].[17,18]

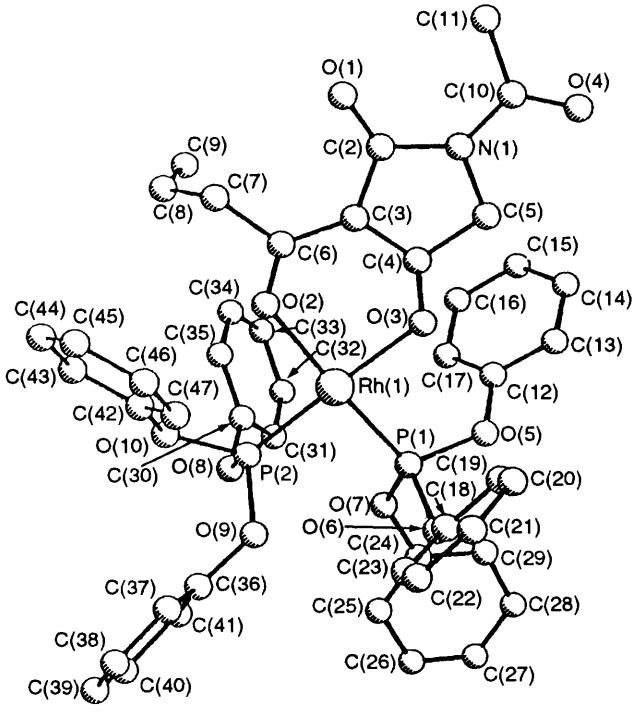


Fig. 1 Crystal structure of the complex $[Rh(abta)\{P(OPh)_3\}_2]$ **3** with the atom numbering scheme

Table 4 Selected bond distances (Å) and angles (°) for $[Rh(abta)\{P(OPh)_3\}_2]$ **3** with standard deviations in parentheses

Rh(1)–P(1)	2.146(3)	C(4)–O(3)	1.24(1)
Rh(1)–P(2)	2.132(4)	C(5)–N(1)	1.45(1)
Rh(1)–O(2)	2.088(7)	C(6)–C(7)	1.51(1)
Rh(1)–O(3)	2.061(8)	C(6)–O(2)	1.24(1)
C(2)–C(3)	1.45(2)	C(7)–C(8)	1.47(2)
C(2)–N(1)	1.41(1)	C(8)–C(9)	1.35(2)
C(2)–O(1)	1.21(1)	C(10)–C(11)	1.50(2)
C(3)–C(4)	1.41(1)	C(10)–N(1)	1.36(1)
C(3)–C(6)	1.42(2)	C(10)–O(4)	1.20(1)
C(4)–C(5)	1.51(2)		
P(1)–Rh(1)–P(2)	89.8(1)	C(2)–C(3)–C(6)	129(1)
P(1)–Rh(1)–O(2)	175.3(2)	C(3)–C(2)–N(1)	108(1)
P(1)–Rh(1)–O(3)	89.2(2)	C(3)–C(2)–O(1)	128(1)
P(2)–Rh(1)–O(2)	93.0(2)	O(1)–C(4)–N(1)	129(1)
P(2)–Rh(1)–O(3)	178.4(2)	C(3)–C(6)–O(2)	121(1)
O(2)–Rh(1)–O(3)	88.1(3)	C(7)–C(6)–O(2)	115(1)
C(4)–C(5)–N(1)	105(1)	C(3)–C(7)–C(8)	121(1)
C(5)–C(4)–O(3)	120(1)	C(6)–C(7)–C(8)	116(1)
C(3)–C(4)–O(3)	132(1)	C(7)–C(8)–C(9)	122(2)
C(3)–C(4)–C(5)	108(1)	C(2)–N(1)–C(5)	110(1)
C(2)–C(3)–C(4)	108(1)	C(1)–N(1)–C(10)	118(1)
C(4)–C(3)–C(6)	123(1)	C(2)–N(1)–C(10)	131(1)

Experimental

Reagents and physical measurements

All experiments were carried out in Schlenk tubes under nitrogen using standard vacuum-line procedures. Solvents were analytical grade and distilled under nitrogen from sodium–benzophenone (toluene, diethyl ether), sodium (pentane), $Mg(OMe)_2$ (methanol) or CaH_2 (dichloromethane). [^{13}C]Carbon monoxide was obtained from Amersham International. Infrared spectra were recorded in CH_2Cl_2 solution between CaF_2 windows on a Perkin-Elmer 886 spectrometer, ^{1}H, ^{13}C and ^{31}P-{^{1}H} NMR spectra on Bruker AC 200, WM 200, WM 250 or AMX 400 NMR spectrometers. The ^{1}H and ^{31}P chemical shifts are referenced to external standards $SiMe_4$ and H_3PO_4 (85% in water), respectively. Elemental analyses were performed in the Department of Chemistry, University of Liverpool.

Syntheses

The compound Habta was synthesised by the method previously described.[9] The complexes [Rh(acac)(CO)$_2$] and [RhCl(PPh$_3$)$_3$] were prepared as described in the literature[19,20] and [Rh(acac)(CO)(PPh$_3$)] as described below.

[Rh(acac)(CO)(PPh$_3$)]. A solution of [RhCl(PPh$_3$)$_3$] (0.688 g, 0.74 mmol) in toluene (15 cm^3) was stirred under CO when it became yellow (*ca.* 1 min). Under nitrogen 1 equivalent of acetylacetone (76 μl) and NaOMe (1.5 cm^3 of a 0.49 mol dm^{-3} MeOH solution, 0.74 mmol) were added. The solution was concentrated and filtered through Celite to remove NaCl. Addition of pentane precipitated a yellow powder, which was collected, washed with water, diethyl ether and pentane and dried under vacuum.

Reactions leading to complexes **1**–**4** are quantitative (IR, NMR spectroscopy); however, substantial losses are encountered during recrystallisation due to the high solubility of the compounds in common organic solvents.

Table 5 Crystal data and data-collection parameters for complex **3**

Formula	$C_{46}H_{42}NO_{10}P_2Rh$
M	933.69
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal dimensions/mm	0.4 × 0.3 × 0.5
Crystal colour	Yellow
a/Å	18.312(3)
b/Å	20.888(7)
c/Å	11.500(3)
α/°	92.56(3)
β/°	93.36(2)
γ/°	83.97(2)
U/Å^3	4364(2)
Z	4
D_c/g cm^3	1.421
F(000)	1920
Diffractometer	Rigaku AFC6S
Beam width/mm	1.00
μ(Mo-Kα)/cm^{-1}	5.12
Scan mode	ω–2θ
2θ range/°	5–50
Scan width/°	1.57 + 0.30 tan θ
λ(Mo-Kα)/Å	0.710 69
No. data collected	12 043
No. unique data used	11 518
R_{int}	0.0077
Range h,k,l	0–22; −25 to 25, −14 to 14
No. unique data used	6267 [$I > 3\sigma(I)$]
Absorption correction	Empirical (based on azimuthal scans)
Weighting scheme, w	$1/\sigma^2(F)$
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.066
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.076

[Rh(abta)(CO)$_2$] 1. Solid Habta (0.082 g, 0.386 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (0.100 g, 0.386 mmol) in CH_2Cl_2 (10 cm^3). The light green solution was stirred for 1 h and then evaporated to dryness to give a red–light green dichroic solid. Dissolution in heptane followed by slow evaporation of the solvent (*ca.* 1 week) under a stream of nitrogen gave very thin light green needles of complex **1**, which sublime under vacuum like [Rh(acac)(CO)$_2$] (Found: C, 39.0; H, 3.5; N, 4.0. $C_{12}H_{12}NO_6Rh$ requires C, 39.0; H, 3.3; N, 3.8%).

[Rh(abta)(CO){P(OPh)$_3$}] 2. The complex [Rh(acac)(CO)$_2$] (0.100 g, 0.386 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and addition of P(OPh)$_3$ (101.2 μl, 0.386 mmol) dissolved in CH_2Cl_2 (5 cm^3) to the stirred solution resulted in the rapid liberation of CO. The compound Habta (0.082 g, 0.386 mmol) was added followed by evaporation to dryness. The resulting oil was washed with a little pentane and methanol, dried under vacuum and crystallised on standing (Found: C, 52.0; H, 4.3; N, 2.0. $C_{29}H_{27}NO_8PRh\cdot H_2O$ requires C, 52.0; H, 4.4; N, 2.1%).

[Rh(abta){P(OPh)$_3$}$_2$] 3. The complex [Rh(acac)(CO)$_2$] (0.100 g, 0.386 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and addition of P(OPh)$_3$ (250 μl, 0.953 mmol) to the stirred solution resulted in the rapid liberation of CO. The compound Habta (0.082 g, 0.386 mmol) was added followed by concentration to 1.5 cm^3. Layering with pentane (10 cm^3) afforded yellow crystals of complex **3**, which were washed three times with cold pentane (3 cm^3) and dried under vacuum (Found: C, 59.0; H, 4.6; N, 1.5. $C_{46}H_{42}NO_{10}P_2Rh$ requires C, 59.2; H, 4.5; N, 1.5%).

[Rh(abta)(CO)(PPh$_3$)] 4. The complex [Rh(acac)(CO)$_2$] (0.100 g, 0.386 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and addition of PPh$_3$ (0.103 g, 0.393 mmol) to the stirred solution resulted in the rapid liberation of CO. The compound Habta (0.082 g, 0.386 mmol) was added, the solution filtered, concentrated to 5 cm^3 and methanol (5 cm^3) added. Concentration under a stream of nitrogen while heated in a water-bath at 60 °C gave yellow crystals. After decanting the supernatant, these were washed with a little cold methanol and dried under vacuum (0.165 g, 71%) (Found: C, 57.4; H, 4.4; N, 2.1. $C_{29}H_{27}NO_5PRh$ requires C, 57.7; H, 4.5; N, 2.3%).

[Rh(abta)(CO)(PPh$_3$)$_2$] 5. This complex was prepared similarly to **4** starting from [Rh(acac)(CO)$_2$] (0.100 g, 0.386 mmol), PPh$_3$ (0.210 g, 0.800 mmol) and Habta (0.082 g, 0.386 mmol). The filtered solution was concentrated to 5 cm^3 and heptane (8 cm^3) added. Concentration under a stream of nitrogen while heated in a water-bath at 60 °C gave yellow crystals. After decanting the supernatant, these were washed three times with pentane (2 cm^3) and dried under vacuum (0.268 g, 80%) (Found: C, 65.4; H, 4.9; N, 1.6. $C_{47}H_{42}NO_5P_2Rh$ requires C, 65.2; H, 4.9; N, 1.6%).

X-Ray crystallography

The crystal data and data-collection parameters are summarised in Table 5. The intensities of three representative reflections measured after every 150 showed no decay. The Rh and P atoms were located by direct methods and the remaining non-hydrogen atoms by Fourier methods. The TEXSAN structure analysis package was used.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were not refined. The final electron-density map showed residual peaks of 0.67 (maximum) and −0.59 (minimum) e Å^{-3}. There were no significant differences between the two molecules in the asymmetric unit. Atom scattering factors were taken from ref. 22. The diagram was

Table 6 Atomic coordinates for [Rh(abta){P(OPh)$_3$}$_2$] **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	0.976 90(5)	0.245 91(5)	0.020 00(7)	C(34)	0.811 9(7)	0.127 8(6)	−0.191(1)
Rh(2)	0.481 67(5)	0.249 87(5)	0.534 71(7)	C(35)	0.825 8(6)	0.190 6(6)	−0.162 9(9)
P(1)	0.940 7(2)	0.251 0(2)	0.194 7(2)	C(36)	0.819 6(7)	0.429 3(6)	0.024(1)
P(2)	0.884 2(2)	0.310 9(2)	−0.031 9(2)	C(37)	0.851 0(9)	0.484 6(8)	−0.001(1)
P(3)	0.445 2(2)	0.252 8(2)	0.708 5(3)	C(38)	0.805(1)	0.538 8(9)	−0.019(1)
P(4)	0.390 9(2)	0.318 0(2)	0.483 7(3)	C(39)	0.733(1)	0.539 8(9)	−0.017(1)
O(1)	1.210 7(5)	0.115 8(4)	−0.242 0(7)	C(40)	0.700(1)	0.489 2(9)	0.007(1)
O(2)	1.012 4(4)	0.232 8(4)	−0.149 5(6)	C(41)	0.746 5(8)	0.428 0(7)	0.027(1)
O(3)	1.067 2(5)	0.185 0(4)	0.074 0(6)	C(42)	0.934 6(6)	0.361 8(5)	−0.219 7(9)
O(4)	1.305 4(5)	0.042 4(4)	0.068 6(7)	C(43)	0.922 8(7)	0.361 2(6)	−0.339(1)
O(5)	0.976 7(4)	0.191 5(4)	0.271 6(6)	C(44)	0.976 7(8)	0.381 9(7)	−0.404(1)
O(6)	0.957 9(4)	0.309 4(4)	0.286 1(6)	C(45)	1.037(1)	0.404 2(8)	−0.351(1)
O(7)	0.854 6(4)	0.253 1(4)	0.209 6(5)	C(46)	1.048 5(8)	0.406 5(7)	−0.232(1)
O(8)	0.803 5(4)	0.286 2(3)	−0.038 5(6)	C(47)	0.995 3(7)	0.385 1(6)	−0.166(1)
O(9)	0.869 5(5)	0.374 6(4)	0.048 9(6)	C(48)	0.672 4(7)	0.107 0(6)	0.559(1)
O(10)	0.878 6(5)	0.339 2(4)	−0.161 6(6)	C(49)	0.614 9(7)	0.155 5(6)	0.513(1)
O(11)	0.571 1(5)	0.185 3(4)	0.583 8(6)	C(50)	0.618 5(6)	0.161 4(5)	0.394 4(9)
O(12)	0.518 7(5)	0.240 2(4)	0.365 4(6)	C(51)	0.680 8(8)	0.118 9(6)	0.359(1)
O(13)	0.798 6(5)	0.030 1(4)	0.565 9(7)	C(52)	0.780 6(7)	0.048 4(6)	0.471(1)
O(14)	0.705 0(5)	0.109 8(4)	0.262 0(7)	C(53)	0.825 5(8)	0.033 3(7)	0.368(1)
O(15)	0.468 3(5)	0.306 8(4)	0.803 4(6)	C(54)	0.572 7(7)	0.205 3(6)	0.325(1)
O(16)	0.475 4(4)	0.192 1(4)	0.782 7(6)	C(55)	0.584 6(7)	0.215 1(6)	0.199(1)
O(17)	0.359 0(4)	0.260 4(4)	0.722 4(6)	C(56)	0.520 6(9)	0.200 9(7)	0.118(1)
O(18)	0.392 3(4)	0.346 8(4)	0.356 5(6)	C(57)	0.502(1)	0.134 0(9)	0.116(1)
O(19)	0.374 9(4)	0.379 3(4)	0.569 1(6)	C(58)	0.530 5(7)	0.336 7(6)	0.786(1)
O(20)	0.309 0(4)	0.295 7(4)	0.467 6(6)	C(59)	0.600 3(8)	0.307 4(6)	0.797(1)
N(1)	1.219 4(6)	0.094 2(5)	−0.045 9(8)	C(60)	0.659 4(8)	0.339 5(7)	0.783(1)
N(2)	0.714 0(6)	0.087 1(5)	0.456 2(8)	C(61)	0.652 5(8)	0.401 4(7)	0.756(1)
C(2)	1.185 0(7)	0.122 3(6)	−0.147(1)	C(62)	0.583(1)	0.434 1(8)	0.747(1)
C(3)	1.118 4(7)	0.161 4(6)	−0.115(1)	C(63)	0.520 7(8)	0.401 8(7)	0.762(1)
C(4)	1.112 4(7)	0.157 8(6)	0.007(1)	C(64)	0.479 5(7)	0.127 0(6)	0.740(1)
C(5)	1.176 5(8)	0.113 3(6)	0.054(1)	C(65)	0.534 1(8)	0.085 6(7)	0.790(1)
C(6)	1.066 9(7)	0.199 6(6)	−0.186(1)	C(66)	0.537 1(9)	0.021 2(8)	0.751(1)
C(7)	1.077 9(7)	0.204 9(6)	−0.314(1)	C(67)	0.491 4(9)	0.000 5(7)	0.666(1)
C(8)	1.017(1)	0.187(1)	−0.394(2)	C(68)	0.436 5(9)	0.041 8(7)	0.618(1)
C(9)	0.992(1)	0.129(1)	−0.393(2)	C(69)	0.429 2(7)	0.107 8(6)	0.654(1)
C(10)	1.285 6(7)	0.058 7(6)	−0.028(1)	C(70)	0.318 6(7)	0.265 8(6)	0.824(1)
C(11)	1.333 0(8)	0.040 6(7)	−0.129(1)	C(71)	0.247 3(7)	0.290 9(6)	0.807(1)
C(12)	0.980 0(7)	0.127 1(6)	0.234(1)	C(72)	0.201 8(7)	0.296 6(6)	0.902(1)
C(13)	1.037 0(7)	0.089 1(6)	0.283(1)	C(73)	0.228 5(8)	0.279 4(7)	1.007(1)
C(14)	1.045 4(8)	0.024 2(7)	0.249(1)	C(74)	0.300 0(8)	0.253 9(7)	1.024(1)
C(15)	0.998 1(9)	0.001 3(7)	0.168(1)	C(75)	0.348 2(7)	0.247 2(6)	0.931(1)
C(16)	0.938 7(9)	0.039 2(8)	0.121(1)	C(76)	0.453 3(7)	0.376 3(6)	0.320(1)
C(17)	0.931 1(8)	0.103 7(7)	0.156(1)	C(77)	0.500 1(8)	0.405 5(7)	0.397(1)
C(18)	1.020 4(7)	0.340 3(6)	0.282(1)	C(78)	0.559(1)	0.434 6(8)	0.345(1)
C(19)	1.089 6(9)	0.305 7(7)	0.304(1)	C(79)	0.562(1)	0.430 6(9)	0.232(2)
C(20)	1.150(1)	0.341 1(8)	0.306(1)	C(80)	0.521(1)	0.403 2(8)	0.154(1)
C(21)	1.143(1)	0.405 2(8)	0.290(1)	C(81)	0.456 9(8)	0.374 8(7)	0.198(1)
C(22)	1.073(1)	0.436 5(9)	0.270(1)	C(82)	0.315 4(6)	0.426 1(5)	0.568(1)
C(23)	1.013 2(9)	0.401 6(8)	0.263(1)	C(83)	0.296 9(8)	0.463 1(7)	0.475(1)
C(24)	0.817 6(7)	0.260 6(6)	0.313(1)	C(84)	0.237(1)	0.514 6(8)	0.485(1)
C(25)	0.758 3(9)	0.305 5(7)	0.312(1)	C(85)	0.204 3(8)	0.523 9(7)	0.586(1)
C(26)	0.717(1)	0.311 5(8)	0.416(1)	C(86)	0.224 8(9)	0.489 2(8)	0.677(1)
C(27)	0.737 3(8)	0.275 7(7)	0.505(1)	C(87)	0.281 8(8)	0.438 2(7)	0.670(1)
C(28)	0.794 9(9)	0.231 5(7)	0.504(1)	C(88)	0.298 9(6)	0.232 5(5)	0.433 3(9)
C(29)	0.836 2(7)	0.222 2(6)	0.405(1)	C(89)	0.251 6(7)	0.202 2(6)	0.495(1)
C(30)	0.794 7(7)	0.221 1(6)	−0.070(1)	C(90)	0.238 6(8)	0.137 9(7)	0.462(1)
C(31)	0.749 9(7)	0.190 9(6)	−0.003(1)	C(91)	0.274 3(8)	0.107 0(7)	0.369(1)
C(32)	0.738 0(8)	0.129 0(7)	−0.033(1)	C(92)	0.321 6(7)	0.139 4(6)	0.311(1)
C(33)	0.767 7(8)	0.096 2(6)	−0.126(1)	C(93)	0.335 1(6)	0.199 7(6)	0.343 1(9)

produced using PLUTO.[23] A list of fractional atomic coordinates is given in Table 6.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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