

# Synthesis and characterisation of two novel Rh(I) carbene complexes: Crystal structure of [Rh(acac)(CO)(L<sub>1</sub>)]

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## Abstract

The [Rh(acac)(CO)(L)] (acac = acetylacetonato; L<sub>1</sub> = 1,3-bis-(2,6-diisopropylphenyl)imidazolinyldiene and L<sub>2</sub> = 1,3-bis-(2,4,6-trimethylphenyl)imidazolinyldiene) complexes were prepared by the action of the parent carbene on [Rh(acac)(CO)<sub>2</sub>] in THF. The crystal structure characterisation of [Rh(acac)(CO)(L<sub>1</sub>)] revealed a slightly distorted square planar geometry with the carbene ligand orientated almost perpendicular to the equatorial plane; an elongated *trans* Rh–O bond of 2.0806(18) Å reflecting the considerable *trans*-influence of the carbene ligand. By measuring the CO stretching frequencies in a range of [Rh(acac)(CO)(L)] complexes (L = CO, L<sub>1</sub>, L<sub>2</sub>, PPh<sub>3</sub>, P<sup>n</sup>Bu<sub>3</sub>, P(O–2,4'-Bu<sub>2</sub>–Ph)<sub>3</sub>) the following electron donating ability series was established: L<sub>1</sub> ~ L<sub>2</sub> ~ P<sup>n</sup>Bu<sub>3</sub> > PPh<sub>3</sub> > P(O–2,4'-Bu<sub>2</sub>–Ph)<sub>3</sub> > CO; indicating the carbenes investigated in this study to have a similar electronic *cis*-influence as trialkyl phosphines. Both complexes do not display hydroformylation activity towards 1-hexene in the absence of added phosphine or phosphite ligands under the conditions investigated (P = 60; T = 85 °C). In the presence of a phosphine or phosphite ligand the resulting hydroformylation catalysis was identical to that observed for [Rh(acac)(CO)<sub>2</sub>] and the corresponding ligand and subsequent high-pressure <sup>31</sup>P NMR studies confirmed substitution of the carbene ligand under these conditions.

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## 1. Introduction

The behaviour of organometallic complexes is critically linked to the ligand system to which they are coordinated. Ligand properties can be tuned to produce complexes displaying very specific characteristics in terms of chemical reactivity and selectivity in catalytic processes as well as to exhibit desirable physical properties such as solubility in certain media. In this regard metal carbene complexes [1–5] have attracted much attention in the last decade since they provide an extra handle for functionalisation on the catalyst. *N*-heterocyclic carbenes are considered to be better electron donating ligands than phosphines [6,7] making them an

attractive ligand class for possible application in homogeneous catalysis.

As part of an extensive investigation [8–10] into the catalytic properties of organometallic complexes in the field of homogeneous catalysis, two [Rh(acac)(CO)(L)] complexes (L<sub>1</sub> = 1,3-bis-(2,6-diisopropylphenyl)imidazolinyldiene and L<sub>2</sub> = 1,3-bis-(2,4,6-trimethylphenyl)imidazolinyldiene) were synthesised as catalyst precursors. In this paper, we report the crystal structure of [Rh(acac)(CO)(L<sub>1</sub>)] and high-pressure <sup>31</sup>P NMR evidence that the rhodium–carbene bond is cleaved under hydroformylation reaction conditions.

## 2. Experimental

All solvents used were purified by standard procedures and air sensitive preparations were carried out

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under a positive nitrogen pressure. The carbene ligands were prepared according to a literature procedure [11].

### 2.1. Synthesis of $[Rh(acac)(CO)(L)]$ complexes

Deprotonation of the respective imidazolium chlorides was performed as described in the literature [11]; addition of a stoichiometric amount of  $[Rh(acac)(CO)_2]$  to this solution resulted in the formation of the desired complexes in good yields.

$[Rh(acac)(CO)(L_1)]$ : ( $\nu(CO)/CH_2Cl_2/cm^{-1}$ ) 1963;  $^1H$  ( $CDCl_3$ ): 1.26 (d, 4 $\times$   $CH_3$ ,  $^3J_{H-H} = 6.9$  Hz,  $L_1$ ), 1.33 (d, 4 $\times$   $CH_3$ ,  $^3J_{H-H} = 6.9$  Hz,  $L_1$ ), 1.78 (s,  $CH_3$ , acac), 1.79 (s,  $CH_3$ , acac), 3.41 (sept, 4 $\times$   $CH(CH_3)_2$ ,  $^3J_{H-H} = 6.9$  Hz,  $L_1$ ), 3.99 (s, 2 $\times$   $CH_2$ ,  $L_1$ ), 5.17 (s,  $CH$ , acac), 7.23 (d, 4 $\times$  *m*-CH,  $L_1$ ), 7.37 (t, 2 $\times$  *p*-CH,  $L_1$ );  $^{13}C$ : 23.74 (s, 4 $\times$   $CH_3$ ,  $L_1$ ), 26.40 (s, 4 $\times$   $CH_3$ ,  $L_1$ ), 27.50 (s, 1 $\times$   $CH_3$ , acac), 27.78 (s, 1 $\times$   $CH_3$ , acac), 28.52 (s, 4 $\times$   $CH(CH_3)_2$ ,  $L_1$ ), 53.92 (s, 2 $\times$   $CH_2$ ,  $L_1$ ), 124.40 (s, 4 $\times$  *m*-C,  $L_1$ ), 128.80 (s, 4 $\times$  *o*-C,  $L_1$ ), 136.98 (s, 2 $\times$  *ipso*-C,  $L_1$ ), 147.15 (s, 2 $\times$  *p*-C,  $L_1$ ), 184.55 (s, 1 $\times$  C, acac), 186.40 (s, 1 $\times$  C, acac), 190.44 (d, 1 $\times$   $C\equiv O$ ,  $^1J_{Rh-C} = 82.5$  Hz), 210.75 (d, 1 $\times$  C-carbene,  $^1J_{Rh-C} = 53.6$  Hz). *Anal. calc.* for  $C_{33}H_{45}N_2O_3Rh$ : C, 63.86; H, 7.31; N, 4.51. Found: C, 64.18; H, 7.40; N, 4.57%.

$[Rh(acac)(CO)(L_2)]$ : ( $\nu(CO)/CH_2Cl_2/cm^{-1}$ ) 1958;  $^1H$  ( $CDCl_3$ ): 1.74 (s,  $CH_3$ , acac), 1.80 (s,  $CH_3$ , acac), 2.29 (s, 2 $\times$  *p*- $CH_3$ ,  $L_2$ ), 2.39 (s, 4 $\times$  *o*- $CH_3$ ,  $L_2$ ), 3.92 (s, 2 $\times$   $CH_2$ ,  $L_2$ ), 5.16 (s,  $CH$ , acac), 6.92 (s, 4 $\times$  *m*-CH,  $L_2$ );  $^{13}C$ : 18.49 (s, 4 $\times$  *o*- $CH_3$ ,  $L_2$ ), 21.09 (s, 2 $\times$  *p*- $CH_3$ ,  $L_2$ ), 26.36 (s, 1 $\times$   $CH_3$ , acac), 27.62 (s, 1 $\times$   $CH_3$ , acac), 50.97 (s, 2 $\times$   $CH_2$ ,  $L_2$ ), 100.08 (s, 1 $\times$   $CH$ , acac), 129.33 (s, 4 $\times$  *m*-C,  $L_2$ ), 136.43 (s, 4 $\times$  *o*-C,  $L_2$ ), 136.71 (s, 2 $\times$  *ipso*-C,  $L_2$ ), 137.55 (s, 2 $\times$  *p*-C,  $L_2$ ), 184.15 (s, 1 $\times$  C, acac), 186.73 (s, 1 $\times$  C, acac), 190.31 (d, 1 $\times$   $C\equiv O$ ,  $^1J_{Rh-C} = 82.0$  Hz), 207.29 (d, 1 $\times$  C-carbene,  $^1J_{Rh-C} = 53.3$  Hz). *Anal. calc.* for  $C_{27}H_{33}N_2O_3Rh$ : C, 60.44; H, 6.20; N, 5.22. Found: C, 60.35; H, 6.53; N, 5.46%.

### 2.2. Crystallography

Intensity data for  $[Rh(acac)(CO)(L_1)]$  were collected at 293(2) K on a Siemens SMART CCD diffractometer using Mo  $K\alpha$  (0.71073 Å) radiation [12]. Individual frames were collected using the  $\omega$ -scan technique and the first 50 frames were recollected after completion to correct for decay of which none was observed. All reflections were merged and integrated using SAINT [13] and corrected for Lorentz, polarisation and absorption effects using SADABS [14]. The structure was solved by the direct method and the positions of the non-H atoms determined from consecutive Fourier maps and refined through full-matrix least-squares cycles using the SHELXS97 [15] and SHELXL97 [16] software package with  $\sum(|F_o| - |F_c|)^2$  being minimised. The hydrogen atoms

were calculated as riding on the parent C atoms (alkyl = 0.96 Å, aryl = 0.93 Å) and refined with an overall temperature factor, all non-H atoms were refined anisotropically. The graphics were done using the Diamond Visual Crystal Structure Information System software [17].

### 2.3. Catalysis

A 300 ml Parr autoclave was charged with the respective rhodium–carbene complex (0.25 mM) and 1-hexene (3 M) in toluene. The autoclave was then heated to 85 °C and pressurised with 60 bar synthesis gas ( $H_2:CO$ , 1:1) for 2 h. End of run catalytic performance was derived from ballast vessel pressure drops and GC analysis.

### 2.4. Spectroscopy

All IR spectra were recorded as  $CH_2Cl_2$  solutions in a variable length solution cell on a Bruker Equinox 55 FTIR instrument equipped with a KBr beamsplitter and controlled by an external computer using OPUS software for acquisition, analysis and manipulation of data. Signal detection was done with a DTGS detector and 32 scans per spectrum were performed using a 10 kHz scanner velocity with no optical filtering.

The  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer using standard pulse sequences at 303 K unless otherwise stated. Chemical shifts are reported in ppm ( $\delta$ ).  $^1H$  NMR spectra were calibrated on the residual  $CHCl_3$  peak at 7.25 ppm,  $^{13}C$  NMR spectra on the  $CDCl_3$  carbon at 77.0 ppm and the  $^{31}P$  NMR spectra relative to an external standard of 85%  $H_3PO_4$  at 0 ppm. All high-pressure experiments were performed in a 10 mm high-pressure Roe cell without spinning. The samples were prepared by transferring a mixture of  $[Rh(acac)(CO)(L)]$  and the phosphine/ phosphite in toluene (1.5 ml toluene + 1.0 ml toluene- $d_8$ ) to the HP-NMR cell. The cell was flushed with argon, closed and pressurised to 20 bar at room temperature with syngas ( $H_2:CO = 1:1$ ). Before recording the spectra, the HP-NMR cell was shaken for 10 min in a mechanical vortex shaker in order to maximise the amount of syngas dissolved in the mixture and to allow the mixture to equilibrate.

## 3. Results and discussion

### 3.1. Synthesis and characterisation

The carbene ligands were synthesised according to established procedures and Rh–carbene complexes were synthesised without significant problems as detailed in

Section 2. The  $^1\text{H}$  NMR spectra of the compounds are very diagnostic with all signals well resolved.

Two methyl groups of the *iso*-propyl substituents on the phenyl rings of the  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_1)]$  complex are diastereotopic and appear as two sets of doublets that couple to the neighbouring CH in the  $^1\text{H}$  NMR spectrum. In the corresponding  $^{13}\text{C}$  NMR spectrum, two singlets are observed for the *iso*-propyl methyl groups which are consistent with this observation. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic assignments are consistent with those previously reported for the uncoordinated carbene ligand [11]. The methyl groups of the acac ligand are in different environments as shown by their magnetic nonequivalency. Two sets of doublets centred at 190.44 ( $^1J_{\text{Rh-C}} = 82.5$  Hz) and 210.75 ppm ( $^1J_{\text{Rh-C}} = 53.6$  Hz) were attributed to the carbonyl and carbene carbons, respectively.

In the  $^1\text{H}$  NMR spectrum of  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_2)]$  all four *ortho* methyl substituents on the phenyl rings resonate as a single signal indicating magnetic equivalence associated with free rotation around the *N*-phenyl bonds. Two sets of doublets centred at 190.31 ( $^1J_{\text{Rh-C}} = 82.0$  Hz) and 207.29 ppm ( $^1J_{\text{Rh-C}} = 53.3$  Hz) were attributed to the carbonyl and carbene carbons, respectively. Both Rh–carbene coupling constants compare well with those in previously reported systems [5].

### 3.2. Crystallography

The numbering scheme and thermal displacement ellipsoids are shown in Fig. 1 and selected geometrical parameters are given in Table 1.

The structure of  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_1)]$  shows the complex to exhibit a slightly distorted square planar geometry with the carbene,  $\text{L}_1$ , coordinated through the carbene carbon as expected. The Rh–O bonds of 2.0806(18) and 2.058(2) Å clearly reflect the larger *trans*-influence of the carbene as compared to that of

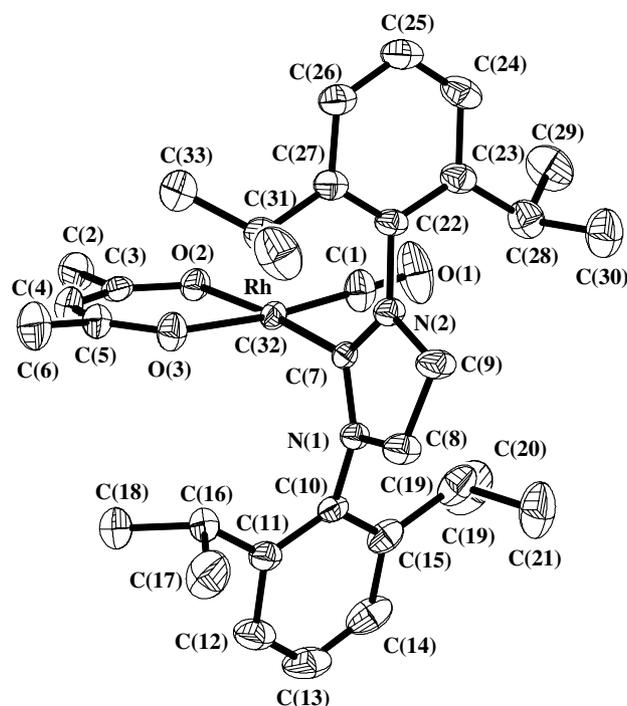


Fig. 1. Numbering scheme and thermal ellipsoids (30% probability) for  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_1)]$ . Hydrogen atoms were omitted for clarity.

the CO ligand, respectively. As indicated by the N(2)–C(7)–Rh–C(1) torsion angle of  $76.5(3)^\circ$  the imidazolium ring of the carbene ligand is orientated almost perpendicular to the coordination plane in accordance with the preferred coordination mode for these molecules. Even though a significant steric demand is expected from the carbene ligand both the C(1)–Rh–C(7) and the C(7)–Rh–O(3) angles of  $90.52(12)^\circ$  and  $90.57(9)^\circ$  indicate only a moderate distortion from the ideal  $90^\circ$ . This observations seems to suggest that the bulky parts of the carbene ligand, i.e., the bis(1,6-diisopropyl-phenyl) substituents, are removed from the inner Rh

Table 1  
Selected geometrical parameters for  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_1)]$

Bond (Å)	Angle ( $^\circ$ )	Torsion angle ( $^\circ$ )			
Rh–O2	2.0806(18)	C1–Rh–O2	90.96(11)	N2–C7–Rh–C1	76.5(3)
Rh–O3	2.058(2)	C1–Rh–O3	174.31(12)	C9–N2–C22–C23	82.0(3)
Rh–C1	1.780(3)	C1–Rh–C7	90.52(12)	C8–N1–C10–C11	79.9(3)
Rh–C7	1.975(3)	O2–Rh–O3	88.45(8)	C17–C16–C11–C12	68.5(4)
C1–O1	1.160(4)	C7–Rh–O2	174.71(9)	C18–C16–C11–C12	–54.3(4)
O2–C3	1.269(3)	C7–Rh–O3	90.57(9)	C20–C19–C15–C14	41.4(4)
O3–C5	1.282(4)	O1–C1–Rh	177.6(3)	C21–C19–C15–C14	–84.3(4)
C3–C4	1.379(4)	N1–C7–Rh	124.04(17)	C29–C28–C23–C24	–45.8(4)
C5–C4	1.392(4)	N1–C7–N2	106.4(2)	C30–C28–C23–C24	76.4(4)
N1–C7	1.353(3)	N2–C7–Rh	129.47(19)	C32–C31–C27–C26	–78.0(4)
N1–C8	1.471(3)			C33–C31–C27–C26	45.1(4)
N1–C10	1.446(3)				
N2–C7	1.348(3)				
N2–C9	1.475(3)				
N2–C22	1.444(3)				

Table 2  
Comparison of geometrical parameters and CO stretching frequencies in [Rh(acac)(CO)(L)] complexes

L	Rh–L	Rh–CO	Rh–O <sub>CO</sub>	Rh–O <sub>L</sub>	$\nu(\text{CO})$ (CHCl <sub>3</sub> )	Ref.
L <sub>1</sub>	1.975(3)	1.780(3)	2.058(2)	2.0806(18)	1963	TW
L <sub>2</sub>					1958	TW
P <sup><i>i</i></sup> Bu <sub>3</sub>					1961	TW
CO		1.75(2)	2.06(2)		2012	[19]
		1.76(2)	2.05(2)		2084	
PPh <sub>3</sub>	2.244(2)	1.801(8)	2.029(5)	2.087(4)	1984	[20]
PPh <sub>2</sub> Fc <sup>a</sup>	2.2331(11)	1.799(4)	2.027(3)	2.072(3)	1980	[21]
	2.2375(13)	1.800(4)	2.038(3)	2.068(3)		
P(NC <sub>4</sub> H <sub>4</sub> ) <sub>3</sub>	2.166(1)	1.826(3)	2.016(2)	2.054(2)	2012 (KBr)	[22]
P(NC <sub>4</sub> H <sub>4</sub> )Ph <sub>2</sub>	2.223(1)	1.817(2)	2.033(2)	2.078(2)	1990	[23]
P(OPh) <sub>3</sub>	2.170(1)	1.823(3)	2.040(2)	2.063(2)	2006	[23]
P(O–2,4- <sup><i>t</i></sup> Bu <sub>2</sub> –Ph) <sub>3</sub>					2007	TW

<sup>a</sup> Two independent molecules in the unit cell.

coordination sphere to such an extent as not to influence it significantly. This concept is supported by the C(9)–N(2)–C(22)–C(23) and C(8)–N(1)–C(10)–C(11) torsion angles of 82.0(3)° and 79.9(3)°, respectively, indicate that both phenyl rings are orientated almost perpendicular with respect to the imidazolium ring of the carbene. Furthermore the *iso*-propyl groups are orientated in such a way that the hydrogen atoms are pointing towards the equatorial plane describe by the ligands around the rhodium atom minimising the steric demand of the carbene ligand. The *iso*-propyl substituents are all orientated very similar with respect to the phenyl rings, see appropriate torsion angles in Table 1, with a staggered conformation exhibited.

Based on the comparative structural data in Table 2 all bonds are within normal ranges for this class of compound. The Rh–O bond *trans* to the carbene is very similar to that found *trans* to phosphine ligands confirming the large *trans*-influence of these ligands. In accordance with known literature [18] the CO stretching frequencies seem to indicate that the electron donating capability of the carbene ligands is larger than for a triaryl phosphine and comparable to that of a trialkyl phosphine.

### 3.3. Catalysis

The activity towards hydroformylation of 1-hexene has been evaluated using [Rh(acac)(CO)(L<sub>2</sub>)] as catalyst precursor with and without added PPh<sub>3</sub> and P(O–2,4-<sup>*t*</sup>Bu<sub>2</sub>–Ph)<sub>3</sub> as auxiliary ligands. No catalyst activity towards the hydroformylation of 1-hexene was observed using [Rh(acac)(CO)(L)] (L = L<sub>1</sub> and L<sub>2</sub>) in the absence of an additional ligand. It was found though that the catalytic activity observed in the presence of the auxiliary ligand corresponds to that of using [Rh(acac)(CO)<sub>2</sub>] as catalyst precursor with the respective ligand. All autoclave experiments thus indicate that no additional beneficial effect was derived from the presence of the carbene in the catalyst precursor.

In order to elucidate the behaviour of the compounds in the presence of a phosphorous donor ligand high-pressure <sup>31</sup>P NMR spectroscopic studies were conducted. These experiments indicated that the rhodium–carbene complexes described in this paper are not stable under hydroformylation reaction conditions and appear to be liberated. Reaction of [Rh(acac)(CO)(L<sub>2</sub>)] with an excess of PPh<sub>3</sub> results in the formation of a [Rh(acac)(L<sub>2</sub>)(PPh<sub>3</sub>)] complex as suggested by the appearance of a doublet at 34.5 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 123 Hz) in the <sup>31</sup>P NMR spectrum. In the presence of 20 bar synthesis gas (H<sub>2</sub>/CO, 1:1) the signal at 34.5 ppm disappeared with the appearance of two doublets at 36.9 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 140 Hz) and 44.3 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 151 Hz), respectively. The doublet at 36.9 ppm corresponds to the formation of the well known hydroformylation rhodium–phosphine precursor [HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [24]. The resonance at 44.3 ppm is thought to be a non-hydride rhodium–carbene complex tentatively assigned as [Rh(CO)<sub>3</sub>(L<sub>2</sub>)(PPh<sub>3</sub>)]<sup>+</sup>. On increasing the temperature from 30 to 100 °C the intensity of the signal corresponding to the rhodium–carbene complexes decreased and finally disappeared. The displacement of the carbene appears to be irreversible as upon cooling and re-acquiring the spectrum the signal at 44.3 ppm did not reappear. Similarly, reaction of [Rh(acac)(CO)(L<sub>2</sub>)] with P(O–2,4-<sup>*t*</sup>Bu<sub>2</sub>–Ph)<sub>3</sub> in the presence of syngas results in the formation of three doublets in the <sup>31</sup>P NMR spectrum at 154.2 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 264 Hz), 137.3 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 223 Hz) and 134.7 ppm (<sup>1</sup>J<sub>Rh–P</sub> = 249 Hz), respectively. The latter two doublets correspond to the formation of complexes of the type [HRh(CO)<sub>3</sub>(P(O–2,4-<sup>*t*</sup>Bu<sub>2</sub>–Ph)<sub>3</sub>)] and [HRh(CO)<sub>2</sub>(P(O–2,4-<sup>*t*</sup>Bu<sub>2</sub>–Ph)<sub>3</sub>)<sub>2</sub>] as described in the literature [9]. Rhodium–hydride signals were observed in the <sup>1</sup>H NMR spectrum which corresponded to the non-carbene ligated rhodium–phosphite complexes. The signal at 154.2 ppm is thought to be a complex of the type [Rh(CO)<sub>3</sub>(P(O–2,4-<sup>*t*</sup>Bu<sub>2</sub>–Ph)<sub>3</sub>)(L<sub>2</sub>)]<sup>+</sup>. In accordance with the behaviour in the

corresponding  $\text{PPh}_3$  study the intensity of the signal at 154.2 ppm decreased and disappeared irreversibly with increasing temperature. No rhodium–carbene–hydride complexes were observed. The cleavage of the rhodium–carbene bond is currently attributed to hydride-transfer to the coordinated carbene but would require additional studies to prove unambiguously.

The observations made during the current study were surprising since it has been shown previously that Rh–carbene complexes do display hydroformylation activity in the absence of phosphines and phosphites [25,26]. In all of these systems though the catalyst precursor also contained either chloride or bromide ligands that might influence the final composition/stability of the activated catalytic species and in such a way account for the difference in catalytic behaviour.

#### 4. Supplementary material

Full crystallographic details for  $[\text{Rh}(\text{acac})(\text{CO})(\text{L}_1)]$  have been deposited with the Cambridge Crystallographic Data Centre, CCDC 264388.

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- [12] Empirical formula:  $\text{RhC}_{33}\text{H}_{45}\text{N}_2\text{O}_3$ ; FW: 620.62; Crystal system: Monoclinic; Space group:  $P2_1/n$ ;  $a = 12.3484(17)$  Å;  $b = 21.096(3)$  Å;  $c = 13.2520(18)$  Å;  $\beta = 109.812(3)^\circ$ ;  $V = 3247.9(8)$  Å<sup>3</sup>;  $Z = 4$ ;  $\mu = 0.558$  mm<sup>-1</sup>;  $T_{\text{max}}/T_{\text{min}}$ : 0.967/ 0.912; Crystal size:  $0.29 \times 0.23 \times 0.18$  mm;  $\theta$  limit: 2.53 to 28.28; Index ranges:  $-15 \leq h \leq 16$ ,  $-28 \leq k \leq 27$ ,  $-17 \leq l \leq 16$ ; Collected reflections: 27330; Independent reflections: 8058;  $R_{\text{int}}$ : 0.0925; Observed reflections [ $I > 2\sigma I$ ]: 5160; Data/ restraints/parameters: 8058/0/363; GoF: 0.937;  $R/wR$  ( $I > 2\sigma I$ ): 0.0400/0.0827;  $R/wR$  (all data): 0.0804/0.0932;  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ : 0.306/−0.615 e Å<sup>-3</sup>.
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