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Synthesis and structural characterisation of rhodium hydride complexes bearing N-heterocyclic carbene ligands

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Abstract

Addition of excesses of N-heterocyclic carbenes (NHCs) IEt_2Me_2, $I^iPr_2Me_2$ or ICy (IEt_2Me_2 = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene; $I^iPr_2Me_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; ICy = 1,3-dicyclohexylimidazol-2-ylidene) to $[HRh(PPh_3)_4]$ (**1**) affords an isomeric mixture of $[HRh(NHC)(PPh_3)_2]$ (NHC = IEt_2Me_2 (*cis*-/*trans*-**2**), $I^iPr_2Me_2$ (*cis*-/*trans*-**3**), ICy (*cis*-/*trans*-**4**)) and $[HRh(NHC)_2(PPh_3)]$ (IEt_2Me_2 (*cis*-/*trans*-**5**), $I^iPr_2Me_2$ (*cis*-/*trans*-**6**), ICy (*cis*-/*trans*-**7**)). Thermolysis of **1** with the aryl substituted NHC, 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ($IMesH_2$), affords the bridging hydrido phosphido dimer, $[\{(PPh_3)_2Rh\}_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ (**8**), which is also the reaction product formed in the absence of carbene. When the rhodium precursor was changed from **1** to $[HRh(CO)(PPh_3)_3]$ (**9**) and treated with either IMes (=1,3-dimesitylimidazol-2-ylidene) or ICy, the bis-NHC complexes *trans*-$[HRh(CO)(IMes)_2]$ (**10**) and *trans*-$[HRh(CO)(ICy)_2]$ (**11**) were formed. In contrast, the reaction of **9** with $I^iPr_2Me_2$ gave $[HRh(CO)(I^iPr_2Me_2)_2]$ (*cis*-/*trans*-**12**) and the unusual unsymmetrical dimer, $[(PPh_3)_2Rh(\mu\text{-}CO)_2Rh(I^iPr_2Me_2)_2]$ (**13**). The complexes *trans*-**3**, **8**, **10** and **13** have been structurally characterised.

Keywords: *N*-heterocyclic carbenes; Hydride ligands; Rhodium complexes

1. Introduction

Metal phosphine hydride complexes play a key role in many catalytic reactions including alkene hydroformylation and alkene and ketone hydrogenation [1]. It is therefore somewhat surprising that despite the plethora of examples of metal complexes in which one or more phosphine ligands have been replaced by N-heterocyclic carbenes (NHCs) (both for studies of fundamental reactions as well as for catalytic applications) [2], only a relatively small proportion of these are NHC metal hydride species [3]. Some members of this group show particularly interesting reactivity patterns involving reductive elimination of NHC and hydride to afford imidazolium salts [3e], 'abnormal' carbene binding through C5 rather than the expected C2 link [3f,3h,3s] and intramolecular C–H bond activation [3b,3g,3n,3t,3u,3v]. It is via this latter pathway, that the two reported examples of rhodium NHC hydride complexes have been prepared by Nolan and co-workers [3a,3r]. Herein, we now report the use of $[HRh(PPh_3)_4]$ and $[HRh(CO)(PPh_3)_3]$ as precursors for new N-alkyl and N-aryl substituted NHC hydride complexes of rhodium.

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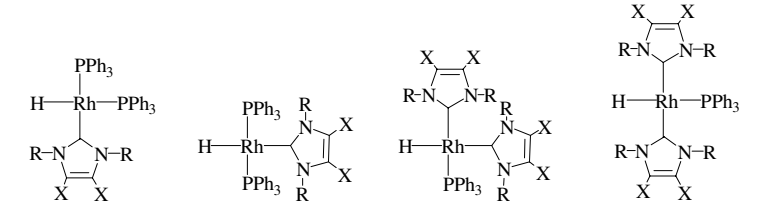
2. Results and discussion

2.1. Reactivity of $[HRh(PPh_3)_4]$ with N-alkyl substituted N-heterocyclic carbenes

Treatment of $[HRh(PPh_3)_4]$ (**1**) with excess of the N-alkyl substituted NHCs IEt_2Me_2, $I^iPr_2Me_2$ or ICy (Scheme 1) proceeded rapidly at room temperature in thf or benzene to afford a mixture of *cis* and *trans* mono- and bis-NHC complexes, $[HRh(NHC)(PPh_3)_2]$ (NHC = IEt_2Me_2 (**2**); $I^iPr_2Me_2$ (**3**); ICy (**4**)) and $[HRh(NHC)_2(PPh_3)]$ (NHC = IEt_2Me_2 (**5**); $I^iPr_2Me_2$ (**6**); ICy (**7**)). Monitoring the reaction progress by ^1H NMR spectroscopy revealed that in each case, all four isomers were formed immediately, although the mono species predominate. The concentrations of the bis-NHC products increased over the course of a few days at room temperature.

Ultimately, the relative ratio of the four possible isomers was found to be dependent on both the nature and number of equivalents of carbene employed [4]. Thus, for example, reaction between **1** and 4 equivalents of $I^iPr_2Me_2$ gave a 1:4.9:1.4:1.2 ratio of *cis*-**3**, *trans*-**3**, *cis*-**6** and *trans*-**6** after 48 h at room temperature (Fig. 1), whilst in the same time, reaction of **1** with ICy (4 equiv.) gave *trans*-**4**, *cis*-**7** and *trans*-**7** in a ratio of 1:2.9:33.8, with no evidence for *cis*-**4** (this isomer is formed upon reaction with fewer equivalents of ICy). Assignment of the products and their relative stereochemistries was readily achieved by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Thus, for example, *cis*- and *trans*-**3** displayed hydride resonances at δ −6.10 (ddd, $^2J_{HP\,trans}$ = 111.9 Hz, $^1J_{HRh}$ = 30.2 Hz, $^2J_{HP\,cis}$ = 24.7 Hz) and δ −10.13 (dt, $^2J_{HP\,cis}$ = 25.4 Hz, $^1J_{HRh}$ = 10.4 Hz), respectively, along with corresponding phosphorus signals at δ 41.6 (dd, $^1J_{PRh}$ = 138.9 Hz, $^2J_{PP}$ = 23.0 Hz) and 49.7 (dd, $^1J_{PRh}$ = 148.5 Hz, $^2J_{PP}$ = 23.0 Hz) for *cis*-**3** and δ 42.7 (d, $^1J_{PRh}$ = 176.4 Hz) for *trans*-**3**. The bis-carbene species *cis*- and *trans*-**6** displayed hydride signals with one less coupling (δ −9.54, dd, $^2J_{HP}$ = 32.2 Hz, $^1J_{HRh}$ = 15.4 Hz; δ −5.43, dd, $^2J_{HP}$ = 121.0 Hz, $^1J_{HRh}$ = 34.6 Hz). The reduction in the size of $^1J_{PRh}$upon changing from a *trans*-P–Rh–P to *trans*-P–Rh–NHC arrangement was noted previously by Lappert and co-workers [5] as being due to higher *trans*-influence of the NHC relative to PR_3.



Scheme 1. Products from reaction of **1** with IEt_2Me_2, $I^iPr_2Me_2$ or ICy.

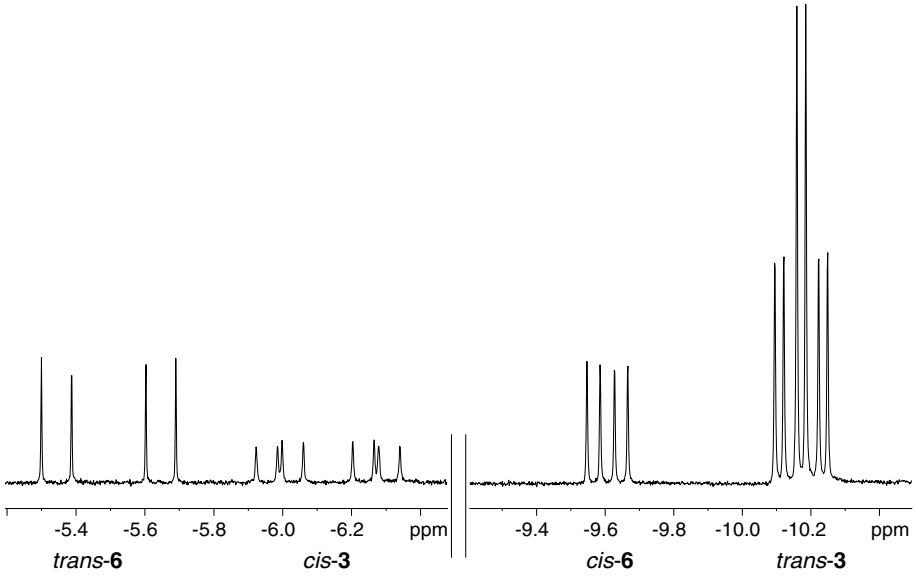


Fig. 1. ^1H NMR spectrum (400 MHz, benzene-d_6) showing hydride resonances from *cis*- and *trans*-**3** and *cis*- and *trans*-**6**.

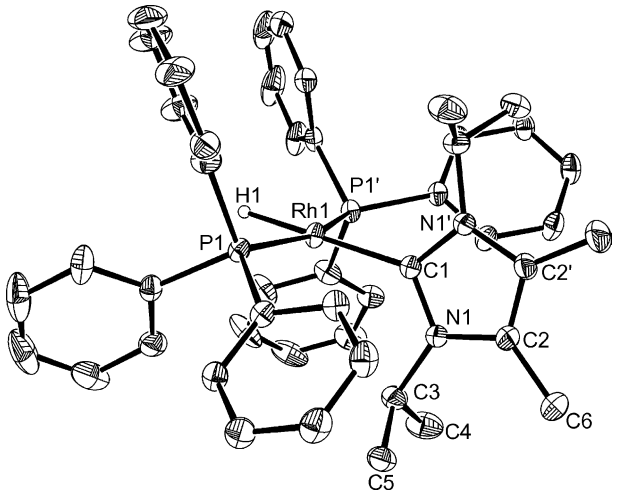


Fig. 2. Molecular structure of *trans*-**3** showing labelling scheme used. Primed labelled atoms related to those in the asymmetric unit by the $-x$, y, $1/2 - z$ symmetry operation. Ellipsoids represented at 30% probability level. Disorder omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for *trans*-[HRh(I^{i}Pr$_2$Me$_2$)(PPh$_3$)$_2$] (*trans*-**3**)

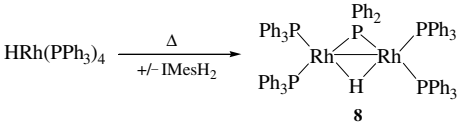
Rh(1)–P(1)	2.2368(4)	Rh(1)–P(1)′	2.2368(4)
Rh(1)–C(1)	2.068(2)		
C(1)–Rh(1)–P(1)	99.804(13)	P(1)–Rh(1)–P(1)′	160.39(3)
C(1)–Rh(1)–P(1)′	99.804(13)		

Primed labelled atoms related to those in the asymmetric unit by the $-x$, y, $-z$ symmetry operation.

Addition of only one equivalent of I^{i}Pr$_2$Me$_2$ to **1** facilitated the isolation of *trans*-**3** crystals suitable for X-ray crystallography. The X-ray structure (Fig. 2) revealed a highly distorted square planar geometry with P–Rh–P and NHC–Rh–P angles of 160.39(3)° and 99.804(13)°, respectively (Table 1). The Rh–carbene bond length (2.068(2) Å) is marginally longer than that found in *cis*-[ClRh(IMes)(PPh$_3$)$_2$] (2.0527(14) Å), presumably reflecting the stronger *trans* influence of hydride versus chloride [6].

2.2. Formation and structural characterisation of [{(PPh$_3$)$_2$Rh}$_2$(μ-H)(μ- PPh$_2$)] (**8**)

In contrast to the facile reactions observed between **1** and IEt$_2$Me$_2$, I^{i}Pr$_2$Me$_2$ and ICy, no reaction was observed between **1** and one equivalent of the saturated N-aryl carbene ligand 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (IMesH$_2$) at room temperature. However, heating at 70 °C for 4 days in thf afforded the bridging phosphido hydride complex [{(PPh$_3$)$_2$Rh}$_2$(μ-H)(μ-PPh$_2$)] (**8**), which was isolated in 38% yield (Scheme 2). Further investigation revealed that **8** was formed upon thermolysis of **1** even in the absence of added



Scheme 2. Formation of [{(PPh$_3$)$_2$Rh}$_2$(μ-H)(μ-PPh$_2$)] (**8**).

NHC. Characterisation of **8** was provided by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and X-ray crystallography. Thus, the ^{1}H NMR spectrum displayed a complex multiplet for the bridging hydride at δ −8.81, while the ^{31}P{^{1}H} NMR spectrum showed a strongly downfield shifted triplet of triplet of triplets for the bridging phosphido ligand, at δ 174.1 (the chemical shift being consistent with a strong metal–metal interaction [7]), a position similar to that reported by Jones [8] for the related di-*tert*-butylphosphido complex, [{(PH^{t}Bu$_2$)(CO)Rh}$_2$(μ-H)(μ-P^{t}Bu$_2$)] and Meek [9] for [(PEt$_3$)$_2$Rh(μ-PPh$_2$)$_2$Rh(COD)]. The ^{31}P{^{1}H} spectrum of **8** was simulated with *g-NMR* [10] and is shown alongside the experimentally determined spectrum in Fig. 3.

The structure of **8** and the presence of a Rh–Rh bond was confirmed unequivocally by an X-ray crystal structure determination, as shown in Fig. 4. Discounting the metal–metal bond, the structure contains two distorted square planar Rh(I) atoms bridged by one hydride and one PPh$_2$ unit (Table 2). This phosphido ligand is bonded asymmetrically to the two rhodium centres as evidenced by the unequal Rh–P bonds lengths (2.2378(5) and 2.2488(5) Å). The Rh–Rh distance of 2.9226(2) Å is somewhat longer than that reported by Jones for the μ-P^{t}Bu$_2$ complex.

2.3. Reactivity of [HRh(CO)(PPh$_3$)$_3$] with NHCs

While the reaction of **1** with NHCs clearly afforded products in which at least some of the starting PPh$_3$ ligands were retained, [HRh(CO)(PPh$_3$)$_3$] (**9**) reacted with both IMes and ICy at room temperature to give the four coordinate bis-carbene species *trans*-[HRh(CO)(IMes)$_2$] (**10**) and *trans*-[HRh(CO)(ICy)$_2$] (**11**) (Scheme 3). The appearance of simple doublet hydride resonances for both compounds (**10**: δ −4.71, $^1J_{HRh}$ = 26.3 Hz; **11**: δ −4.55, $^1J_{HRh}$ = 25.8 Hz) testified to the complete loss of all PPh$_3$ ligands from **9** during these reactions. The ^{13}C{^{1}H} NMR spectra of the two complexes each showed a single low field doublet carbene resonance (**10**: δ 197.7, $^1J_{CRh}$ = 44.1 Hz; **11**: δ 192.5, $^1J_{CRh}$ = 46.0 Hz) confirming the *trans* orientation of the NHC ligands. As expected, a single, strong ν_{CO} IR absorption band was found for each complex (**10**: 1919 cm^{-1}; **11**: 1914 cm^{-1}) [11].

The X-ray crystal structure of **10**, a distorted square planar Rh(I) complex, is shown in Fig. 5 and selected bond lengths and angles are given in Table 3. The molecular structure shows the expected square planar

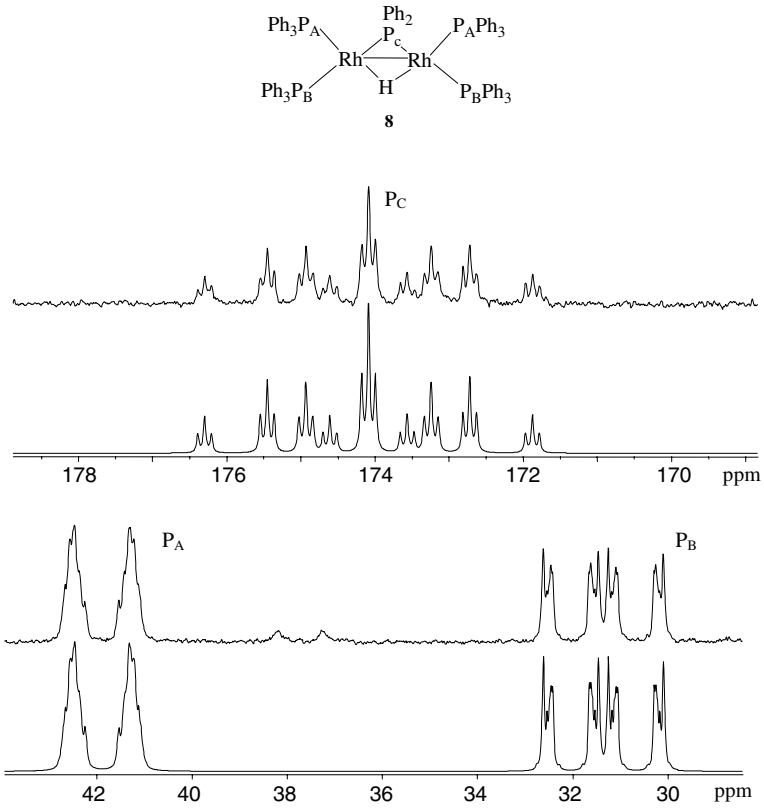


Fig. 3. Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectra (162 MHz) for complex **8**.

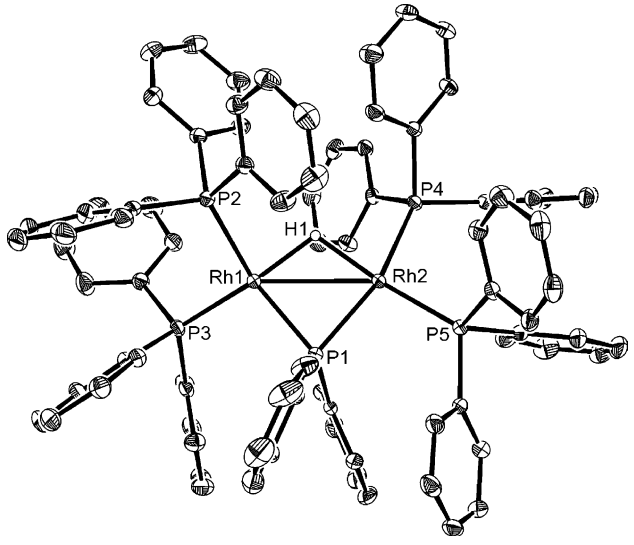
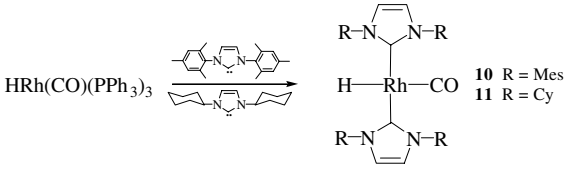


Fig. 4. Molecular structure of **8**. Thermal ellipsoids are shown at the 30% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for [{$(PPh_3)_2Rh$}$_2$(μ-H)(μ-PPh_2)] (**8**)

Rh(1)–P(3)	2.2599(5)	Rh(1)–P(1)	2.2378(5)
Rh(1)–Rh(2)	2.9226(2)	Rh(1)–P(2)	2.3266(5)
Rh(2)–P(5)	2.2454(5)	Rh(2)–P(1)	2.2488(5)
P(1)–Rh(1)–P(3)	101.097(19)	Rh(1)–P(1)–Rh(2)	81.297(16)
P(1)–Rh(1)–P(2)	148.80(2)	P(3)–Rh(1)–P(2)	98.619(19)
P(5)–Rh(2)–P(1)	99.809(18)	P(1)–Rh(1)–Rh(2)	49.515(13)
P(5)–Rh(2)–P(4)	102.269(18)	P(1)–Rh(2)–P(4)	150.255(19)
P(1)–Rh(2)–Rh(1)	49.188(13)	P(5)–Rh(2)–Rh(1)	147.224(14)



Scheme 3. Reactivity of [$HRh(CO)(PPh_3)_3$] (**9**) with IMes or ICy.

coordination around the rhodium centre with a C(2)–Rh–C(23) bond angle of 172.91(7). The Rh–carbene bond lengths (2.0165(16), 2.0191(17) Å) are comparable to those reported for *trans*-[ClRh(CO)(1,3-dibenzylimidazol-2-ylidene)], but somewhat shorter than found in the *trans* isomer of [$ClRh(CO)(IMe)_2$] (IMe = 1,3-dimethylimidazol-2-ylidene) [12].

When **9** was reacted with$I^iPr_2Me_2$ in benzene solution, ^{1}H NMR spectroscopy indicated the formation of a 1:8 mixture of two hydride containing products assigned as *cis*- and *trans*-[$HRh(CO)(I^iPr_2Me_2)_2$] (*cis*-/*trans*-**12**) due to their lack of a $^{2}J_{HP}$ splitting. As expected, the $^{31}P\{^{1}H\}$ NMR spectrum indicated the presence of free PPh_3, but also revealed a lone doublet

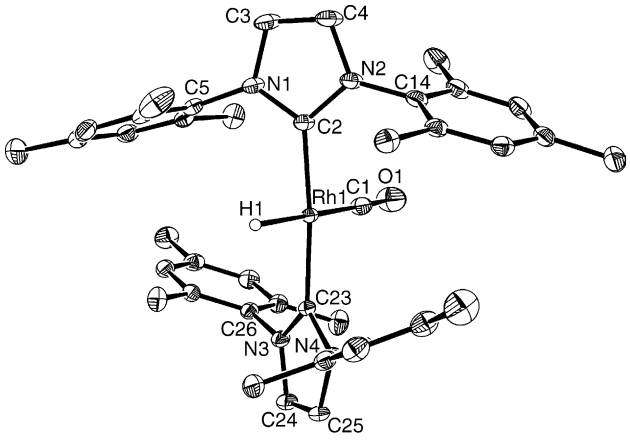


Fig. 5. Molecular structure of **10**. Thermal ellipsoids are shown at the 30% probability level.

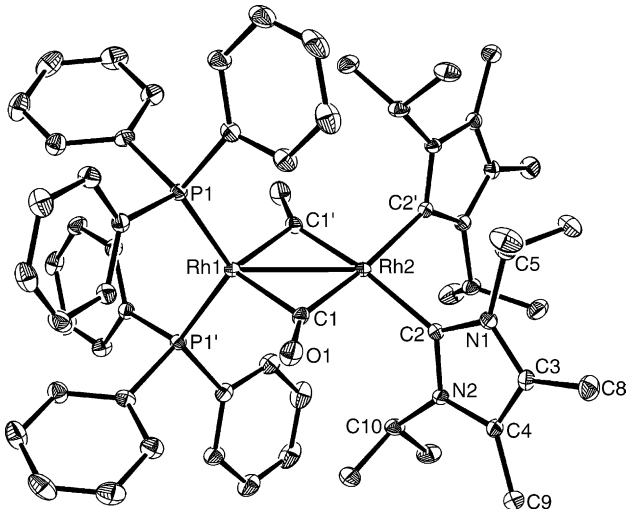


Fig. 6. Molecular structure of **13** showing labelling scheme used. Primed labelled atoms related to those in the asymmetric unit by the $-x$, y, $-z$ symmetry operation. Ellipsoids represented at 30% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for *trans*-[HRh(CO)(IMes)$_2$] (**10**)

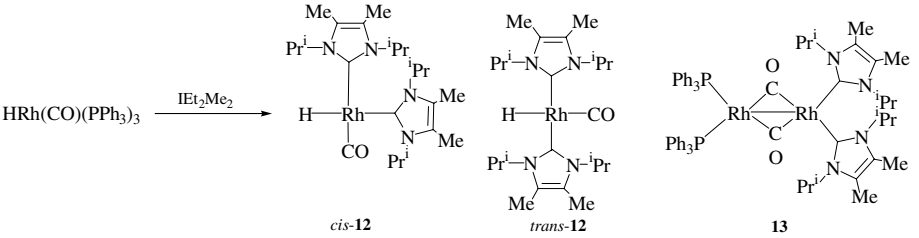
Rh(1)–C(23)	2.0165(16)	Rh(1)–C(1)	1.843(2)
O(1)–C(1)	1.144(3)	Rh(1)–C(2)	2.0191(17)
C(1)–Rh(1)–C(23)	94.61(8)	O(1)–C(1)–Rh(1)	178.5(2)
C(1)–Rh(1)–C(2)	92.41(8)	C(23)–Rh(1)–C(2)	172.91(7)

of doublets signal at δ 37.6 arising from the unsymmetrical carbonyl bridged dimer [(PPh$_3$)$_2$Rh(μ-CO)$_2$Rh-(I^{i}Pr$_2$Me)$_2$] (**13**) (Scheme 4). The structure of this product has been established unambiguously by X-ray crystallography as shown in Fig. 6, which indicates a square planar Rh bis-carbene fragment (C(6)–Rh(2)–C(2) = 94.87(12)°) connected to a distorted tetrahedral Rh(PPh$_3$)$_2$ unit (P(1)-Rh(1)-P(2) = 122.91(3)°) via two bridging CO ligands and a Rh–Rh bond (Table 4). The Rh–Rh distance of 2.6939(3) Å is comparable to that found in [{(PCy$_3$)$_2$Rh}$_2$(μ-CO)$_2${Rh(PCy$_3$)(CO)}] [13], [{(PPh$_3$)$_2$Rh}$_2$(μ-CO)$_2$] [14] and [{(P(O^{i}Pr)$_3$)$_2$Rh}$_2$-(μ-CO)$_2$] [15].

Table 4
Selected bond lengths (Å) and angles (°) for [(PPh$_3$)$_2$Rh(μ-CO)$_2$-Rh(I^{i}Pr$_2$Me$_2$)$_2$] (**13**)

Rh(1)–C(1)′	1.995(3)	Rh(1)–P(1)	2.3019(6)
Rh(1)–P(1)′	2.3019(6)	Rh(2)–C(1)	2.005(3)
Rh(1)–Rh(2)	2.6939(3)	Rh(2)–C(2)′	2.073(2)
Rh(2)–C(1)′	2.005(3)	P(1)–C(25)	1.831(3)
Rh(2)–C(2)	2.073(2)	O(1)–C(1)	1.1570(18)
Rh(1)–C(1)	1.995(3)		
C(1)′–Rh(1)–C(1)	95.64(16)	C(1)′–Rh(1)–P(1)′	107.83(3)
C(1)–Rh(1)–P(1)′	109.60(3)	C(1)′–Rh(1)–P(1)	109.60(3)
C(1)–Rh(1)–P(1)	107.83(3)	P(1)′–Rh(1)–P(1)	122.91(3)
C(1)′–Rh(1)–Rh(2)	47.82(8)	C(1)–Rh(1)–Rh(2)	47.82(8)
P(1)′–Rh(1)–Rh(2)	118.543(16)	P(1)–Rh(1)–Rh(2)	118.543(16)
C(1)–Rh(2)–C(1)′	95.03(16)	C(1)–Rh(2)–C(2)′	168.07(7)
C(1)′–Rh(2)–C(2)′	86.29(9)	C(1)–Rh(2)–C(2)	86.29(9)
C(1)′–Rh(2)–C(2)	168.07(7)	C(2)′–Rh(2)–C(2)	94.87(12)
C(1)–Rh(2)–Rh(1)	47.52(8)	C(1)′–Rh(2)–Rh(1)	47.52(8)
C(2)′–Rh(2)–Rh(1)	132.57(6)	C(2)–Rh(2)–Rh(1)	132.57(6)
O(1)–C(1)–Rh(1)	125.7(3)	O(1)–C(1)–Rh(2)	149.6(3)
Rh(1)–C(1)–Rh(2)	84.663(6)		

Primed labelled atoms related to those in the asymmetric unit by the $-x$, y, $-z$ symmetry operation.



Scheme 4. Reactivity of [HRh(CO)(PPh$_3$)$_3$] with I^{i}Pr$_2$Me$_2$.

3. Conclusions

The rhodium phosphine hydride complexes $[HRh(PPh_3)_4]$ and $[HRh(CO)(PPh_3)_3]$ react with a range of *N*-alkyl and *N*-aryl substituted *N*-heterocyclic carbenes mostly to afford mixtures of products resulting from the substitution of between one and three PPh_3 ligands. It remains to be seen in the few cases in which single isolable products such as *trans*-$[HRh(I^iPr_2Me_2)(PPh_3)_2]$ (*trans*-**3**) and *trans*-$[HRh(CO)(IMes)_2]$ (**10**) are formed, whether these show enhanced reactivity towards small molecules; such studies are in progress.

4. Experimental

4.1. General considerations

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. All solvents were distilled under a nitrogen atmosphere from purple solutions of sodium benzophenone ketyl (toluene, benzene, hexane, thf) or Mg/I_2 (ethanol, methanol). Benzene-d_6 toluene-d_8 and thf-d_8 (Aldrich) were vacuum transferred from potassium. Literature routes or slight modifications thereof were used to prepare $[HRh(PPh_3)_4]$ [16], $[HRh(CO)(PPh_3)_3]$ [16], IMes [17], $IMesH_2$ [18], IEt_2Me_2 [19] and $I^iPr_2Me_2$ [19]. ICy was prepared according to a method described by Nolan [20]. ^1H NMR spectra were recorded on Bruker Avance 300 and 400 MHz NMR spectrometers and referenced to the chemical shifts of residual protio solvent resonances (benzene-d_5 δ 7.15, thf-d_7 δ 3.57). $^{13}C\{^1H\}$ NMR spectra were referenced to benzene-d_6 (δ 128.0) and thf-d_8 (δ 26.2). $^{31}P\{^1H\}$ NMR chemical shifts were referenced externally to 85% H_3PO_4 (δ 0.0). ^1H COSY, ^1H–X (X = ^{13}C, ^{31}P) HMQC and HMBC experiments were performed using standard Bruker pulse sequences. Spectral simulations for $[\{Rh(PPh_3)_2\}_2(\mu\text{-}H)(\mu\text{-}PPh_2)]$ were performed using *g-NMR* [10]. IR spectra were recorded as nujol mulls on a Nicolet Protégé 460 FTIR spectrometer. Elemental analyses were performed at the University of Bath.

4.2. Reaction of **1** with IEt_2Me_2, $I^iPr_2Me_2$ or ICy

In a typical reaction, $[HRh(PPh_3)_4]$ (0.05 g, 0.043 mmol) and free NHC (2–6 equivalents) were loaded into a J. Young's resealable NMR tube in the glovebox. Benzene-d_6 or thf-d_8 (ca. 0.6 mL) was added via vacuum transfer and the reactions followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

4.2.1. Reaction with IEt_2Me_2

Selected NMR data for *cis*-**2**, ^1H NMR (thf-d_8 298 K): δ −5.70 (ddd, $^2J_{HPtrans}$ = 113.0 Hz, $^2J_{HPcis}$ = 25.2 Hz, $^1J_{HRh}$ = 24.7 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 41.4 (dd, $^1J_{PRh}$ = 136.5 Hz, $^2J_{PP}$ = 24.5 Hz), 49.2 (dd, $^1J_{PRh}$ = 148.1 Hz, $^2J_{PP}$ = 24.5 Hz). Selected NMR data for *trans*-**2**, ^1H NMR (thf-d_8 298 K): δ −9.59 (dt, $^2J_{HP}$ = 23.6 Hz, $^1J_{HRh}$ = 11.0 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 45.4 (d, $^1J_{PRh}$ = 175.0 Hz). Selected NMR data for *cis*-**5**, ^1H NMR (thf-d_8 298 K): δ −8.82 (dd, $^2J_{HP}$ = 29.1 Hz, $^1J_{HRh}$ = 15.9 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 54.7 (d, $^1J_{PRh}$ = 159.7 Hz). $^{13}C\{^1H\}$ NMR: δ 185.3 (dd, $^1J_{CRh}$ = 42.2 Hz, $^2J_{CP}$ = 15.6 Hz, Rh–*C*), 197.2 (dd, $^1J_{CRh}$ = 57.0 Hz, $^2J_{CP}$ = 13.8 Hz, Rh–*C*). Selected NMR data for *trans*-**5**, ^1H NMR (thf-d_8 298 K): δ −4.67 (dd, $^2J_{HP}$ = 121.3 Hz, $^1J_{HRh}$ = 35.1 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 38.5 (d, $^1J_{PRh}$ = 135.2 Hz). $^{13}C\{^1H\}$ NMR: δ 199.9 (dd, $^1J_{CRh}$ = 46.1 Hz, $^2J_{CP}$ = 10.1 Hz, Rh–*C*).

4.2.2. Reaction with $I^iPr_2Me_2$

Selected NMR data for *cis*-**3**, ^1H NMR (thf-d_8 298 K): δ −6.10 (ddd, $^2J_{HPtrans}$ = 111.9 Hz, $^1J_{HRh}$ = 30.2 Hz, $^2J_{HPcis}$ = 24.7 Hz, 1H, Rh–H), 6.12 (sept, $^3J_{HH}$ = 7.15 Hz, 2H, C*H* Me_2). $^{31}P\{^1H\}$ NMR: δ 41.6 (dd, $^1J_{PRh}$ = 138.9 Hz, $^2J_{PP}$ = 23.0 Hz), 49.7 (dd, $^1J_{PRh}$ = 148.5 Hz, $^2J_{PP}$ = 23.0 Hz). Selected NMR and analytical data for *trans*-**3**, ^1H NMR (thf-d_8 298 K): δ −10.13 (dt, $^2J_{HPcis}$ = 25.4 Hz, $^1J_{HRh}$ = 10.4 Hz, 1H, Rh–H), 0.71 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 2.13 (s, 6H, NC*Me*), 5.93 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*Me_2). $^{31}P\{^1H\}$ NMR: δ 42.7 (d, $^1J_{PRh}$ = 176.4 Hz). $^{13}C\{^1H\}$ NMR: δ 198.6 (td, $^1J_{CRh}$ = 47.5 Hz, $^2J_{CP}$ = 10.5 Hz, Rh–*C*). Anal. Found: C, 69.9; H, 6.49; N, 3.53%. $C_{47}H_{51}N_2P_2Rh$ (808.72) Calc.: C, 69.80; H, 6.36; N, 3.46. Selected NMR data for *cis*-**6**, ^1H NMR (thf-d_8 298 K): δ −9.54 (dd, $^2J_{HP}$ = 32.2 Hz, $^1J_{HRh}$ = 15.4 Hz, 1H, Rh–H), 5.71 (sept, $^3J_{HH}$ = 7.46 Hz, 2H, C*H*Me_2), 6.09 (sept, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*Me_2). $^{31}P\{^1H\}$ NMR: δ 37.9 (d, $^1J_{PRh}$ = 138.1 Hz). Selected NMR data for *trans*-**6**, ^1H NMR (thf-d_8 298 K): δ −5.43 (dd, $^2J_{HP}$ = 121.0 Hz, $^1J_{HRh}$ = 34.6 Hz, 1H, Rh–H), 6.50 (sept, $^3J_{HH}$ = 7.10 Hz, 4 H, C*H* Me_2). $^{31}P\{^1H\}$ NMR: δ 52.1 (d, $^1J_{PRh}$ = 161.1 Hz). $^{13}C\{^1H\}$ NMR: δ 200.5 (dd, $^1J_{CRh}$ = 45.3 Hz, $^2J_{CP}$ = 11.0 Hz, Rh–*C*).

4.2.3. Reaction with ICy

Selected NMR data for *cis*-**4**, ^1H NMR (thf-d_8 298 K): δ −5.88 (ddd, $^2J_{HPtrans}$ = 112.0 Hz, $^2J_{HPcis}$ = 25.2 Hz, $^1J_{HRh}$ = 30.2 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 42.6 (dd, $^1J_{PRh}$ = 142.9 Hz, $^2J_{PP}$ = 24.5 Hz), 49.2 ($^1J_{PRh}$ = 148.1 Hz, $^2J_{PP}$ = 24.5 Hz). Selected NMR data for *trans*-**4**, ^1H NMR (thf-d_8 298 K): δ −9.49 (dt, $^2J_{HP}$ = 24.7 Hz, $^1J_{HRh}$ = 11.0 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 44.0 (d, $^1J_{PRh}$ = 178.8 Hz). $^{13}C\{^1H\}$ NMR: δ 179.9 (td, $^1J_{CRh}$ = 40.4 Hz, $^2J_{CP}$ = 16.5 Hz, Rh–*C*). Selected NMR data for *cis*-**7**, ^1H NMR (thf-d_8 298 K): δ −9.05 (dd, $^2J_{HP}$ = 32.4 Hz, $^1J_{HRh}$ = 15.4 Hz, 1 H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 53.3 (d, $^1J_{PRh}$ = 160.9 Hz).

Selected NMR data for *trans*-**7**, ^{1}H NMR (thf-d_8 298 K): δ −4.99 (dd, $^2J_{HP}$ = 123.5 Hz, $^1J_{HRh}$ = 35.1 Hz, 1 H, Rh–H). $^{31}P\{^1H\}$ NMR: δ 38.8 (d, $^1J_{PRh}$ = 135.2 Hz). $^{13}C\{^1H\}$ NMR: δ 199.3 (dd, $^1J_{CRh}$ = 44.7 Hz, $^2J_{CP}$ = 11.0 Hz, Rh–*C*).

4.3. Formation of [{Rh(PPh$_3$)$_2$}$_2$(μ-H)(μ-PPh$_2$)] (**8**)

A thf solution of [HRh(PPh$_3$)$_4$] (0.05 g, 0.043 mmol) was heated at 70 °C for 4 days with an equivalent of IMesH$_2$ (0.013 g, 0.043 mmol). Removal of the solvent gave a brown precipitate. Addition of thf/ethanol afforded small red crystals of the dimer [{Rh(PPh$_3$)$_2$}$_2$ (μ-H)(μ-PPh$_2$)] (yield 0.022 g, 38% yield). ^{1}H NMR (thf-d_8 298 K): δ −8.80 (m, 1H, Rh–H–Rh), 7.81–6.15 (m, 70H, PPh). $^{31}P\{^1H\}$ NMR: δ 41.9 (m, J_{PARh} = 195.3 Hz*, $J_{PA'Rh}$ = 7.8 Hz*, $J_{PAPA'}$ = 34.7 Hz*, J_{PAPB} = 28.6 Hz*, $J_{PAPB'}$ = 4.0 Hz*, J_{PAPC} = 15.0 Hz*, P_A), 31.4 (m, J_{PBRh} = 158.2 Hz*, $J_{PB'Rh}$ = 2.9 Hz*, $J_{PBPB'}$ = 2.3 Hz*, J_{PBPA} = 28.6 Hz*, $J_{PB'PA}$ = 4.0 Hz*, J_{PBPC} = 221.3, P_B), 174.1 (ttt, $^1J_{PRh}$ = 136.5 (136.9)* Hz, $^2J_{PPB}$ 221.3 (221.3)* Hz, $^2J_{PPA}$ = 15.5 (15.0)* Hz, Rh–μPPh$_2$–Rh (P_C)). *Coupling constants found by spectral simulation. Anal. Found: C, 69.91; H, 4.89%. $C_{84}H_{71}P_5Rh$ (1441.03) Calc.: C, 70.01; H, 4.97.

4.4. Preparation and characterisation of [HRh(CO)(IMes)$_2$] (**10**)

[HRh(CO)(PPh$_3$)$_3$] (0.025 g, 0.027 mmol) and IMes (0.049 g, 0.16 mmol) were dissolved in thf-d_8 (0.5 mL). Proton NMR spectroscopy indicated that reaction was complete in the time of mixing to afford **10** as the sole product. The solvent was removed in vacuo to give a sticky red-brown precipitate. Addition of EtOH (3 mL) afforded a bright yellow microcrystalline solid (yield 0.019 g, 97%). X-ray quality crystals were grown from a crude benzene solution of the compound (with free carbene and free phosphine present) upon layering with hexane. ^{1}H NMR (thf-d_8 298 K): δ −4.71 (d, 1H, $^1J_{HRh}$ = 26.3 Hz), 1.78 (s, 24H, *o*-C$_6$*Me*$_2$H$_2$Me), 2.37 (s, 12H, *p*-C$_6$Me$_2$H$_2$*Me*), 6.74 (s, 8H, C$_6$Me$_2$*H*$_2$Me), 6.91 (s, 4H, NCH). $^{13}C\{^1H\}$: δ 18.4 (s, *o*-Me), 21.1 (s, *p*-Me), 121.1 (s, N*C*H), 128.9 (s, *m*-*C*H), 136.4 (s, *C*-*o*-Me), 136.8 (s, *C*-*p*-Me), 138.7 (s, N-*C*), 194.5 (d, $^1J_{CRh}$ = 60.7 Hz, Rh–*CO*), 197.7 (d, $^1J_{CRh}$ = 44.1 Hz, Rh–*C*). IR (Nujol, cm^{-1}): 1919 (ν_{CO}). Anal. Found: C, 69.8; H, 6.65; N, 7.56%. $C_{49}H_{43}N_4Rh$ (740.72) Calc.: C, 69.72; H, 6.67; N, 7.56.

4.5. Preparation and characterisation of [HRh(CO)(ICy)$_2$] (**11**)

[HRh(CO)(PPh$_3$)$_3$] (0.025 g, 0.027 mmol) and ICy (0.013 g, 0.056 mmol) were dissolved in thf-d_8 in a J. Young's resealable NMR tube. A $^{31}P\{^1H\}$ NMR spectrum recorded after 16 h at room temperature showed that [HRh(CO)(ICy)$_2$] was the sole product. ^{1}H NMR (thf-d_8 298 K): δ −4.55 (d, 1H, $^1J_{HRh}$ = 25.8 Hz, RhH), 0.77–2.53 (m, 40H, C$_6$H$_{10}$), 5.30 (m, 4H, N–C*H*$_{ipso}$), 7.04 (s, 4H, NC*H*). $^{13}C\{^1H\}$: δ 26.4 (s, C$_6$H$_{11}$), 26.8 (s, C$_6$H$_{11}$), 34.0 (s, C$_6$H$_{11}$), 60.3 (s, N–*C*H$_{ipso}$), 116.2 (s, N*C*H), 192.5 (d, $^1J_{CRh}$ = 46.0 Hz, Rh–*C*), 196.0 (d, $^1J_{CRh}$ = 59.7 Hz, Rh–*C*O). IR (Nujol, cm^{-1}): 1914 (ν_{CO}).

4.6. Formation of [(PPh$_3$)$_2$Rh(μ-CO)$_2$Rh(I^{i}Pr$_2$Me$_2$)$_2$] (**13**)

HRh(CO)(PPh$_3$)$_3$] (0.025 g, 0.027 mmol) and I^{i}Pr$_2$Me$_2$ (0.027 g, 0.17 mmol) were dissolved in benzene-d_6 (0.6 mL) in a J. Young's resealable NMR tube to afford a mixture of *cis*- and *trans*-[HRh(I^{i}Pr$_2$Me$_2$)$_2$-(CO)] in a ratio of 1:8 (^{1}H NMR). The $^{31}P\{^1H\}$ NMR spectrum showed the expected singlet for free PPh$_3$, along with a doublet assigned to [(PPh$_3$)$_2$Rh(μ-CO)$_2$-Rh(IPr$_2$Me$_2$)$_2$]. The solution was concentrated and layered with hexane to afford a few large, dark red crystals of this dimeric complex, which proved suitable for X-ray crystallography. ^{1}H NMR (benzene-d_6 298 K): δ 0.98 (d, 12H, $^3J_{HH}$ = 7.1 Hz, CH*Me*$_2$), 1.26 (d, 12H, $^3J_{HH}$ = 7.1 Hz, CH*Me*$_2$), 1.75 (s, 12H, NCMe), 6.02 (sep, 4H, $^3J_{HH}$ = 7.1 Hz, C*H*Me$_2$), 6.92–7.11 (m, 18H, PPh$_3$), 7.69–7.89 (m, 12H, PPh$_3$). $^{31}P\{^1H\}$ NMR: δ 37.6 (dd, $^1J_{PRh}$ = 236.5 Hz, $^2J_{PRh}$ = 7.7 Hz, Rh–PPh$_3$). $^{13}C\{^1H\}$: δ 11.0 (s, NC*Me*), 21.7 (s, CH*Me*$_2$), 22.3 (s, CH*Me*$_2$), 54.1 (s, *C*HMe$_2$), 124.6 (s, N*C*Me), 135.2 (m, *meta* PC$_6$H$_5$), 141.5 (m, PC$_{ipso}$), 191.2 (d, $^1J_{CRh}$ = 57.0 Hz, Rh–*C* (I^{i}Pr$_2$Me$_2$)). IR (Nujol, cm^{-1}): 1708 (ν_{CO}).

4.7. Crystallography

Single crystals of compounds *trans*-**3**, **10** and **13** were analysed using a Nonius Kappa CCD diffractometer, while data for **8** were obtained on a Bruker SMART at Daresbury, station 9.8. Details of the data collections, solutions and refinements are given in Table 5. The structures were universally solved using SHELXS-97 [21] and refined using full-matrix least squares in SHELXL-97 [21]. Convergence was uneventful, with the following exceptions and points of note.

The asymmetric unit in *trans*-**3** was seen to contain one half of a molecule, with the central ruthenium, carbene carbon and hydride located on a crystallographic 2-fold rotation axis that serves to generate the remainder of the molecule. The hydride was located in the penultimate difference Fourier electron density map and refined at 1.6 Å from the central metal. The phenyl ring based on C19 is disordered over 2 sites, in a 60:40 ratio. Both partial occupancy fragments were refined as rigid hexagons. Atoms in minor component are labelled with suffix 'A'. The bridging hydride located in **8** was refined

Table 5
Crystal data and structure refinement details for compounds *trans*-**3**, **8**, **10** and **13**

Compound	*trans*-**3**	**8**	**10**	**13**
Molecular formula	$C_{47}H_{51}N_2P_2Rh$	$C_{84}H_{71}P_5Rh_2$	$C_{43}H_{47}N_4O$ Rh	$C_{30}H_{35}N_2O$ P Rh
Formula weight	808.75	1441.08	738.76	573.48
T (K)	150(2)	150(2)	150(2)	150(2)
Wavelength	0.71073	0.67750	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$Pbca$	$C2$
a (Å)	24.0740(3)	24.3635(11)	17.2090(1)	18.7420(2)
b (Å)	10.4850(1)	13.4417(6)	19.1070(1)	13.3980(2)
c (Å)	18.6690(2)	21.1106(10)	23.1810(1)	12.5570(1)
β (°)	116.866(1)	95.026(1)		118.493(1)
U (Å^3)	4203.73(8)	6886.9(5)	7622.20(7)	2771.21(6)
Z	4	4	8	4
D_c (g cm^{-3})	1.278	1.390	1.288	1.375
μ (mm^{-1})	0.516	0.641	0.485	0.698
$F(000)$	1688	2960	3088	1188
Crystal size (mm)	$0.25 \times 0.25 \times 0.20$	$0.18 \times 0.10 \times 0.10$	$0.60 \times 0.50 \times 0.40$	$0.50 \times 0.25 \times 0.10$
Theta range for data collection	3.80–27.48	3.30–55.84	3.52–30.04	3.56–28.27
Index ranges	$-31 \leqslant h \leqslant 31$; $-13 \leqslant k \leqslant 13$; $-24 \leqslant l \leqslant 24$	$-34 \leqslant h \leqslant 34$; $-19 \leqslant k \leqslant 19$; $-30 \leqslant l \leqslant 30$	$-24 \leqslant h \leqslant 24$; $-26 \leqslant k \leqslant 26$; $-32 \leqslant l \leqslant 32$	$-24 \leqslant h \leqslant 24$; $-17 \leqslant k \leqslant 17$; $-16 \leqslant l \leqslant 16$
Reflections collected	30096	80730	149425	23814
Independent reflections [it R_{int}]	4803 [0.0342]	20885 [0.0802]	11139 [0.0496]	6654 [0.0472]
Reflections observed [$I > 2\sigma(I)$]	4346	13601	9193	6310
Data completeness	0.995	0.995	0.997	0.990
Absorption correction	Semi-empirical from equivalents	SADABS	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission factors	0.91, 0.88	0.88, 0.81	0.79, 0.76	0.88, 0.57
Data/restraints/parameters	4803/1/270	20885/1/821	11139/0/453	6654/1/317
Goodness-of-fit on F^2	1.055	0.795	1.082	1.057
R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0299, 0.0725	0.0321, 0.0559	0.0338, 0.0876	0.0267, 0.0611
R_1, wR_2 indices (all data)	0.0346, 0.0758	0.0570, 0.0589	0.0455, 0.0977	0.0304, 0.0635
Largest diff. peak and hole (e Å^{-3})	0.414, −0.629	0.560, −0.412	1.025, −0.757	1.022, −0.916

subject to having similar bond distances to each metal centre, while the hydride in **10** was readily located and refined without any restraints.

In compound **13**, the asymmetric unit was also seen to consist of half of a dimer molecule. The remaining portion is generated via a 2-fold crystallographic rotation axis on which both Rh1 and Rh2 are sited. The absolute structure parameter for this structure, which solved in space group $C2$, refined to a value of 0.04(19).

5. Supplementary material

Crystallographic data for compounds *trans*-**3**, **13**, **8** and **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 260100–260103, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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