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# N-Heterocyclic Carbene Rhodium Complexes and Their Reactions with $H_2$ and with CO

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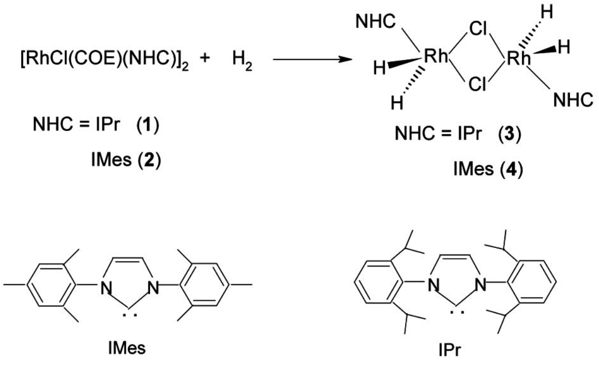
The NHC-$Rh^I$ complexes $[RhCl(COE)(NHC)]_2$ **1** and **2** [COE = cyclooctene, NHC in **1** = *N*,*N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and, in **2**, *N*,*N*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes)] react with $H_2$ in hexane to give the dimeric, mono-carbene dihydrido species $[Rh(H)_2Cl(NHC)]_2$ (NHC = IPr (**3**), IMes (**4**)). In the presence of further NHC, the bis-carbene dihydrido species $Rh(H)_2Cl(NHC)_2$ are formed; a crystal structure of the IPr complex **5** is analogous to that of the known IMes analogue. The dihydride-mixed-carbene species $Rh(H)_2Cl(IPr)(IMes)$ (**5a**) was also observed but not isolated. A benzene solution of **5** under $D_2$ slowly generates the corresponding dideuteride. Reactions of the mono-carbenes (**1**/**3**, or **2**/**4**) with CO in hexane afford the respective dicarbonyl complexes $RhCl(CO)_2(NHC)$ [NHC = IPr (**6**), IMes (**7**)], while CO reactions with the bis-carbene dihydrides give, respectively, the mono-carbonyl complex $RhCl(CO)(IPr)_2$ (**8**) and the known IMes analogue. All the complexes are characterized by elemental analysis, $^1H$ and $^{13}C\{^1H\}$ NMR and IR spectroscopies and, in the case of **5**, by X-ray crystallography. The catalytic activities of **5** and the previously reported $Rh(H)_2Cl(IMes)_2$ for hydrogenation of COE and 1-octene (and isomerization of the latter) are shown to be poor.

## Introduction

Interest in NHC-Rh complexes (NHC = N-heterocyclic carbene) shows no signs of abatement, as can judged by the contents of this special issue of the *Eur. J. Inorg. Chem.*, and other recent publications[1–12] and the references contained therein. Our initial studies in metal-carbene chemistry[13] developed from attempts to replace oxidizable tertiary phosphane ligands in a Ru system that showed catalytic activity for conversion of $N_2O$ to $N_2$ and $O_2$.[14] We later reported that (carbene-phosphanyl)-$Rh^I$ species undergo "standard" oxidative addition of $O_2$ to give $Rh^{III}$-peroxide species,[15] while Crudden and co-workers have recently suggested that such species are best considered as $Rh^I$ with coordinated singlet oxygen.[16] Our studies[13–15] have thus far mainly utilized the simple, unfunctionalized NHCs, *N*,*N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and *N*,*N*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) (see Scheme 1), in syntheses of the RhCl(diene)(NHC) and $[RhCl(COE)(NHC)]_2$ complexes, and reactivities of these complexes with $O_2$ (diene = NBD or COD, and COE = cyclooctene). Because of our interests in catalytic hydrogenation/hydroformylation, we then studied reactions of the $[RhCl(COE)(NHC)]_2$ complexes with $H_2$ and with CO, with an ultimate goal of comparing catalytic activity of such systems with those of classic Rh-tertiary phosphane systems.[17] There is literature on reactions of $H_2$ and CO, and related catalysis, within NHC-$Rh^I$ systems,[5,9,13,18–21] but not specifically with the COE/IPr/IMes precursors, and our studies have led to identification of new species, as well as some findings on catalytic hydrogenation and isomerization of COE and 1-octene. Our findings on the $O_2$ and $H_2$ reactions were first presented at a Canadian Chemistry conference.[22] During the writing of this paper, we heard that Crudden's group had also been studying reactivity of $H_2$, CO, and $N_2$, toward the same NHC-$Rh^I$ species, and their work (with necessarily some overlap) is reported in this journal issue.[23]



Scheme 1. Reactions of **1** and **2** with $H_2$.

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## Results and Discussion

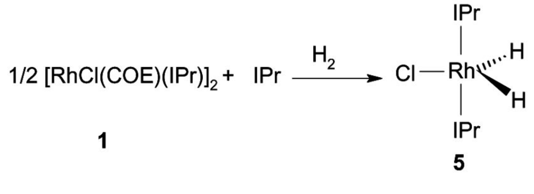
### Reactions Involving $H_2$

Reactions of the yellow complexes $[RhCl(COE)(NHC)]_2$ (**1**, NHC = IPr; **2**, IMes) with $H_2$ at ambient conditions were initially studied in $C_6D_6$, where in-situ $^1H$ NMR spectroscopic data showed the formation of cyclooctane (COA, $\delta$ = 1.50 ppm, br. s) and new Rh-hydride species indicated by a high-field doublet resonance at $\delta$ = –22.78 ppm, $J$ = 27 Hz (from **1**) or a broad singlet at $\delta$ –21.61 ppm (from **2**), conversion being complete in ca. 1 h. Carrying out the reactions in hexane, where **1** and **2** are present as suspensions, allowed for isolation of the respective hydride products $[Rh(H)_2Cl(IPr)]_2$ (**3**) and $[Rh(H)_2Cl(IMes)]_2$ (**4**) in ca. 75% yield (Scheme 1), which were both obtained as yellow solids containing 0.5 molecule COA as solvate. The complexes **3** and **4** were characterized by elemental analysis, and NMR and IR spectroscopies. For **3**, as well as the high-field doublet resonance for the equivalent hydrides, the $^1H$ NMR spectrum (in $C_6D_6$) shows a $\delta$ = 6.43 ppm singlet for the NC*H* proton, a septet signal at $\delta$ = 2.92 ppm for the IPr-methine protons, and doublets at $\delta$ = 1.34 and 1.02 ppm for two types of Me-groups; the signal integrations and $J$ values support the formulation, as well the $^{13}C\{^1H\}$ data, which include a doublet for the carbene carbon at $\delta$ = 182.7 ppm ($J_{RhC}$ = 58 Hz), the normal range for carbene-Rh complexes.[13,24] The hydride resonances are also in the range reported for the hydride ligands of Rh(H)Cl(IMes′)(IMes), where IMes′ is the cyclometallated carbene formed from a methyl group via intramolecular C–H activation,[15,18] and of $Rh(H)_2Cl(IMes)_2$ (see below).[18] For **4**, the $^1H$ NMR spectrum shows also singlets (of correct integrations) at $\delta$ = 6.11 ppm for the NC*H* proton, and at $\delta$ = 2.18 and 2.13 ppm, respectively, for the *p*-Me and *o*-Me groups of the IMes ligands. The expected carbene–carbon resonance of **4** is surprisingly absent in the $^{13}C\{^1H\}$ NMR, although the same absence has been noted for **2**, the precursor complex.[15] This is not understood but the signal is presumably broadened into the base-line by some exchange process, and reflects in some way the relatively labile and weak metal–carbene bond in this system (formation of **4** from **2** is not reversed on subjecting a solution to vacuum). Of note, rapid exchange of N-heterocyclic ligands in various Ag systems, including between dinuclear $Ag_2$ and tetranuclear $Ag_4$ species, is well known.[25]

Complexes **3** and **4** have $\nu_{RhH}$ IR bands at 2124 and 2103 cm$^{-1}$, respectively; these are in the range seen for (hydride-tertiary phosphane)-Rh$^{III}$ species,[26] and so useful comparisons of electronic properties of NHC vs. $PR_3$ ligands cannot be made from these particular IR data. Data on $\nu_{RhH}$ IR bands do not appear to have been noted previously for NHC-containing species. More careful IR studies with measurements in the same media (solid state/solution) for NHC vs. corresponding $PR_3$ complexes could contribute to a better understanding of the electronic properties of the two ligands, which remain debatable, particularly the location of electron density in their complexes with transition metals.[27] Corresponding data on some$\nu_{CO}$ values are discussed below.

We were unable to obtain any useful data for **3** or **4** from either MALDI-TOF- or ESI-mass spectrometry investigations, and thus we have no direct evidence for their dimeric nature. The empirical formulation $Rh(H)_2Cl(NHC)$, implying a four-coordinate Rh$^{III}$ complex, certainly reminded us of Nolan's work on related Rh-NHC species formed by steps involving double C–H activation of the I*t*Bu ligand [I*t*Bu = *N*,*N*-bis(*tert*-butyl)imidazol-2-ylidene], loss of $H_2$, and chloride removal,[19] but the chemistry in the syntheses of **3** and **4** leads us tentatively to the dimeric formulation (as assumed also for the Rh$^I$-precursors $[RhCl(COE)(NHC)]_2$[15,19]).

The monomeric, dihydrido-bis(NHC) complex $Rh(H)_2Cl(IMes)_2$ (**5′**) is a known, crystallographically characterized compound, and was synthesized previously from the room temperature reaction (in THF) of $H_2$ with Rh(H)Cl(IMes′)(IMes),[18] the cyclo-metallated complex noted above. In this work, we synthesized the analogous $Rh(H)_2Cl(IPr)_2$ complex (**5**) in high yield by the room temperature reaction of $H_2$ with a suspension of **1** in hexane in the presence of 1 equiv. of IPr per Rh (Scheme 2). In situ $^1H$ NMR spectroscopic data on the initially formed clear yellow solution revealed complete conversion to **5** (and the COE of **1** to COA), and cooling to 0 °C yielded the light yellow crystalline **5**, which was fully characterized by elemental analysis, IR ($\nu_{RhH}$) and NMR spectroscopy, and X-ray analysis. The $^1H$ NMR spectrum in $C_6D_6$ shows resonances for two equivalent IPr ligands and a doublet at $\delta$ = –22.90 ppm ($J_{RhH}$ = 33 Hz) for two equivalent hydrides; the $^{13}C\{^1H\}$ NMR doublet for the carbene-carbon ($\delta$ = 194.5 ppm, $J_{RhC}$ = 36 Hz) is ca. 12 ppm downfield from that of the dihydrido-monocarbene complex **3**. The high-field hydride $^1H$ NMR signal slowly disappeared when the $C_6D_6$ solution of **5** was frozen, the NMR-tube evacuated, then subjected to a $D_2$ atmosphere, and warmed to room temperature; over 24 h with intermittent shaking of the NMR-tube, the corresponding dideuteride **5-D₂** was formed ($\delta_D$ = –22.96 ppm, br. s), with $^1H$ NMR spectroscopic data of the IPr ligands being the same as those of **5**. The reverse exchange was also demonstrated. The observations establish the reversible nature of $H_2/D_2$ binding possibly to a "$RhCl(IPr)_2$" species, although reactivity via $\eta^2$-$H_2/D_2$ intermediates cannot be ruled out. In this regard, it should be noted that in the conversion of **5** to **5-D₂**, the disappearing $\delta$ = –22.90 ppm hydride doublet of **5** was accompanied by formation of a new doublet at $\delta$ = –22.96 ppm with the same J value of 33 Hz, and this presumably pertains to some isomeric form of **5**; both doublets slowly disappeared as the dideuteride formed. More detailed studies of this conversion are on-



Scheme 2. Formation of $Rh(H)_2Cl(IPr)_2$ (**5**).

going. There is no evidence for C–H activation of an isopropyl methyl group to give a hydrido-alkyl species, similar to that seen for the analogous "RhCl(IMes)$_2$" species.[15,18] The IMes analogue of **5** (the known complex **5′**[18]) was also synthesized in high yield by the procedure used for synthesis of **5**.

X-ray quality crystals of **5** were obtained by slow evaporation of a saturated hexane solution of the complex, the collected crystals being washed with Et$_2$O and dried in vacuo. The structure reveals a hexane/Et$_2$O-solvated, "supposed" trigonal bipyramidal, five-coordinate dihydride complex (Figure 1), analogous to that of the unsolvated Rh(H)$_2$Cl(IMes)$_2$ complex **5′**, where the hydride ligands were located.[18] In our case, the Rh–H hydrides were not located even though residual electron density around the Rh was evident. The two IPr ligands are mutually *trans* [177.1(2)°] and the chloride is almost perpendicular to the IPr ligands [91.43(12)°]; the diisopropylphenyl substituents are twisted by an average of 81.97° with respect to the central imidazole ring. The Rh–C and Rh–Cl bond lengths of 2.029(4) and 2.4083(14) Å are close to those reported for other (C2-carbene)-Rh$^{III}$ complexes (e.g. ref.[2,4,5,9,18,28]). Crudden and co-workers have synthesized complex **5** from the nitrogen complex *trans*-RhCl(N$_2$)(IPr)$_2$, and have also obtained a crystal structure for **5** which co-crystallized with the Rh$^{II}$ complex RhCl$_2$(IPr)$_2$; their determined crystallographic geometrical parameters for a non-solvated crystal of **5** are close to our values, and they were able also to locate the hydrides (Rh–H = 1.45 Å).[23]

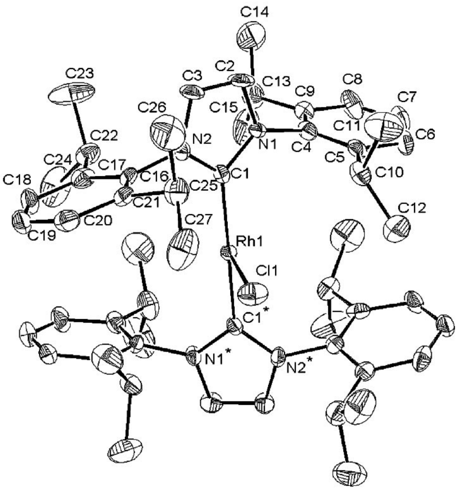


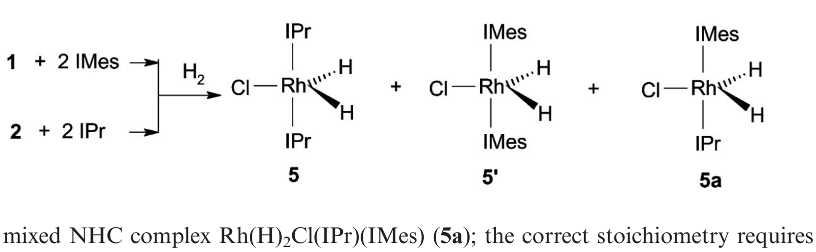
Figure 1. ORTEP diagram of Rh(H)$_2$Cl(IPr)$_2$ (**5**) with 50% probability thermal ellipsoids. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh(1)–C(1) 2.029(4), Rh(1)–Cl(1) 2.4083(14); C(1)–Rh(1)–C(1*) 177.1(2), C(1)–Rh(1)–Cl(1) 91.43(12).

In attempts to make hydrido, mixed-NHC complexes, reactions of [RhCl(COE)(IPr)]$_2$ (**1**) with 1 equiv. of IMes per Rh were examined. In C$_6$D$_6$ at ambient conditions under H$_2$, an in situ mixture of a new mixed-carbene complex Rh(H)$_2$Cl(IPr)(IMes) (**5a**), Rh(H)$_2$Cl(IPr)$_2$ (**5**), and the known Rh(H)$_2$Cl(IMes)$_2$ (**5′**),[18] was obtained (Scheme 3), as judged by the three, respective, high-field doublets at $\delta$ –23.21 ($J_{\text{RhH}}$ = 36 Hz), –22.90 ($J_{\text{RhH}}$ = 33 Hz), and –22.78 ppm ($J_{\text{RhH}}$ = 35 Hz). On the basis of data for the isolated **5** and **5′**, the other $^1$H resonances of the in-situ mixture fit well data for the three Rh species. The integrations of the three hydride signals changed slowly with time, indicating equilibria among the species, and after ca. 6 h, the final ratio of the three products was close to 1:1:1. A synthetic scale reaction in hexane led to isolation of the hexane-soluble **5**, and a mixture of **5a** and **5′** in 25% yield, from which the $^1$H NMR signals for **5a** were assigned (see Experimental); similar solubilities of **5a** and **5′** have thus far thwarted attempts to separate the materials. Not surprisingly, the same chemistry results by reaction of H$_2$ with [RhCl(COE)(IMes)]$_2$ (**2**) in the presence of one equivalent of IPr.

Of note, **5** also reacts rapidly in benzene with O$_2$ to form the dioxygen species RhCl(O$_2$)(IPr)$_2$, which has been isolated by another route and purported by X-ray (O–O = 1.315 Å), IR, Raman, and XAS data, to be a (singlet oxygen)-Rh$^{I}$ complex.[16] We have also structurally characterized the oxygen complex and find an O–O bond length of 1.393 Å,[29] approaching the length for a standard peroxide complex.[15] The nature of this important "discrepancy" is currently under investigation via collaboration with Crudden and co-workers.

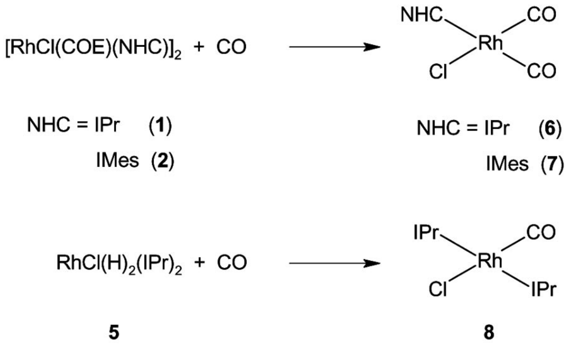
## Reactions Involving CO

Reactions of **1** or **3** in hexane solution with 1 atm of CO at room temperature generated *cis*-RhCl(CO)$_2$(IPr) (**6**), and the IMes analogue **7** was formed from the corresponding CO reactions with **2** or **4**; use of the hydrido species **3** and **4** involved loss of H$_2$, which was detectable in the solution at $\delta_{\text{H}}$ = 4.18 ppm. The CO reaction with **5** gave the biscar-



Scheme 3. Formation of the mixed NHC complex Rh(H)$_2$Cl(IPr)(IMes) (**5a**); the correct stoichiometry requires a factor of 2/3 for each product.

bene complex *trans*-RhCl(CO)(IPr)$_2$ (**8**) (Scheme 4). The CO reactions were instantaneous, and the products were isolated in almost quantitative yields from the hexane solutions as white solids. Complexes **6**–**8** are well characterized by elemental analyses, and NMR and IR spectroscopies. The $^1$H NMR spectroscopic data are straightforward, and the $^{13}$C{$^1$H} data generally so. For **6**, three $^{13}$C{$^1$H} doublets are seen at $\delta = 186.0$ ($J_{\text{Rh–C}} = 54$ Hz), 184.2 ($J_{\text{Rh–C}} = 72$ Hz) and 182.1 ppm ($J_{\text{Rh–C}} = 45$ Hz) for the one carbene-carbon and the two inequivalent carbonyls; signal assignment is not obvious, because $J_{\text{Rh–C}}$ values for the carbene carbon atom are typically in the 35–65 Hz range (e.g.ref.[2,4–7,9,13,15]). Two $\nu_{CO}$ bands at 2073 and 1990 cm$^{-1}$ indicate efficient back-bonding from Rh$^{I}$ to the carbonyl ligands. Other *cis*-RhCl(CO)$_2$(NHC) complexes, made by reactions of CO with RhCl(COD)(NHC), also have symmetric and asymmetric $\nu_{CO}$ bands (KBr) in the 2088–2069 and 2002–1994 cm$^{-1}$ ranges, respectively.[5,30] For **7**, the $^{13}$C{$^1$H} spectrum shows only one doublet at $\delta = 186.0$ ppm ($J_{\text{Rh-C}} = 54$ Hz) for the two carbonyl ligands, and one for the carbene-carbon at $\delta = 179.2$ ppm ($J_{\text{Rh-C}} = 45$ Hz), although two $\nu_{CO}$ IR bands at 2070 and 1990 cm$^{-1}$ are consistent with inequivalent carbonyls, at least in the solid-state structure. This phenomenon has been found in other carbene-carbonyl-Rh complexes.[19] For the mono(carbonyl) complex with two trans NHC ligands (**8**), two $^{13}$C{$^1$H} doublets at $\delta = 189.8$ ($J_{\text{Rh-C}} = 42$ Hz) and 188.1 ppm ($J_{\text{Rh-C}} = 79$ Hz) show the presence of equivalent IPr ligands and one carbonyl, and the single $\nu_{CO}$ band is seen at 1938 cm$^{-1}$. A $\nu_{CO}$ value of 1935 cm$^{-1}$ in CH$_2$Cl$_2$ solution has been recorded for the analogous RhCl(CO)(IMes)$_2$ complex made from the reaction of CO with the cyclometallated complex Rh(H-)Cl(IMes′)(IMes),[18] but the paper does not report any $^{13}$C{$^1$H} data. Reported $\nu_{CO}$ values (cm$^{-1}$) for *trans*-RhCl(CO)(PPh$_3$)$_2$ are 1983 (in KBr)[31] and 1980 (in CHCl$_3$),[32] while values for *cis*-RhCl(CO)$_2$(PPh$_3$), a suggested reaction intermediate, are 2088 and 2002 cm$^{-1}$ (in hexadecane);[32] these phosphane species are the analogues of the carbene complexes **8** (and the IMes analogue[18]), and **6**/**7**, respectively. The IR data, even allowing for the different media, imply that PPh$_3$ is a better $\pi$-acceptor than IPr and IMes in these Rh$^{I}$ complexes, and are consistent with similar data from Herrmann's group that carbenes (vs. tertiary phosphanes) result in higher electron density at a Rh$^{I}$ centre.[5] Contrary to this generally accepted behaviour of the two types of ligands, recent K-edge XAS spectra suggest the opposite for some Ru$^{II}$ systems.[27]



Scheme 4. Reactions of complexes **1**, **2** and **5** with CO; complexes **3** and **4** could be used, respectively, instead of **1** and **2**.

A crystal structure of complex **8** (synthesized from *trans*-RhCl(N$_2$)(IPr)$_2$) is reported elsewhere in an article in this journal issue.[23]

### Catalytic Hydrogenations

Hydrogenation of olefinic substrates using Rh-NHC catalysts, either with[9,33] or without[9,30] ancilliary phosphane ligands, has been reported, but we were unaware of any attempts at such catalysis using characterized Rh-hydrido-NHC complexes as catalyst precursors. Thus, we tested via a few preliminary experiments the Rh(H)$_2$Cl(NHC)$_2$ complexes **5** (NHC = IPr) and **5′** (NHC = IMes) for catalytic hydrogenation of cyclooctene and 1-octene at ambient conditions, and compared data with those we obtained also using the well-known RhCl(PPh$_3$)$_3$ system.[34] However, the Rh-NHC compounds are not useful catalysts. For example, in benzene under conditions given in the Experimental section, conversions of cyclooctene over 24 h even at 45 °C reached only about 15%, and at this temperature the solutions darkened likely due to formation of colloidal metal that eventually precipitated; RhCl(PPh$_3$)$_3$ gave about three times the conversion with no visible signs of decomposition. Much faster consumption of 1-octene was seen (90% in 5 h at room temperature using **5** as catalyst, and in 3 h using **5′**) but the major reaction was isomerization to *cis*- and mainly *trans*-2-octene, followed by slower hydrogenation of the *cis*- and *trans*-isomers, a well known phenomenon;[35] with RhCl(PPh$_3$)$_3$ hydrogenation was complete in ca. 3 h, with only trace isomerization observed. Under Ar at room temperature, complexes **5** and **5′** do catalyze the isomerization but more slowly (ca. 30–40% after 5 h). Our findings generally parallel closely more detailed studies reported by Herrmann et al.,[9] who tested RhCl(COD)(NHC) and [Rh(COD)(NHC)$_2$]$^+$ in toluene for catalytic hydrogenation of cyclohexene and 1-octene; in these systems, addition of PPh$_3$ was needed to generate effective catalysts. Nolan's group has reported low activity for RhCl(IMes)(PPh$_3$)$_2$ for hydrogenation of cyclohexene,[20] but this study was carried out in CH$_2$Cl$_2$ not generally a favoured solvent because hydrogen transfer to the solvent can occur with liberation of HCl.[36] That **5** and **5′** were synthesized under H$_2$, and showed no signs of decomposition under H$_2$ up to 45 °C, implies that under the catalytic conditions an olefin might be replacing at least one of the NHC ligands, this leading to destabilization of the Rh$^{I}$ state and decomposition to metal.

## Conclusions

The carbene-Rh$^{I}$ complexes [RhCl(COE)(NHC)]$_2$, NHC = IPr and IMes, are used to synthesize via reactions with H$_2$: the mono-carbene dihydride complexes [Rh(H)$_2$–

Cl(NHC)]$_2$, NHC = IPr (**3**) and IMes (**4**), the bis-carbene dihydride Rh(H)$_2$Cl(IPr)$_2$ (**5**), which was characterized crystallographically, and the known IMes analogue **5′**. The mixed dihydride, Rh(H)$_2$Cl(IPr)(IMes) was also characterized in situ. Complex **5** undergoes reversible exchange with D$_2$ to form the dideuteride. Complexes **5** and **5′** are not effective precursors for catalytic hydrogenation of cyclooctene and 1-octene. Reactions of CO with the [RhCl(COE)(NHC)]$_2$ or [Rh(H)$_2$Cl(NHC)]$_2$ complexes yield the dicarbonyl compounds RhCl(CO)$_2$(NHC), while the monocarbonyl complex RhCl(CO)(IPr)$_2$ is prepared by reaction of CO with the dihydride **5**. The $\nu_{CO}$ data for these Rh$^I$ complexes support the premise that PPh$_3$ is a better π-acceptor than the NHC ligands.

## Experimental Section

**General:** All manipulations were performed under Ar, using standard Schlenk or glove-box techniques. Reagent grade solvents (Fisher Scientific) were dried using standard procedures, and prior to use were purged with a stream of Ar. Deuterated solvents (Cambridge Isotope Laboratories) were similarly dried, and then distilled under N$_2$ prior to use. Common chemicals were obtained from Fisher Scientific, and were used as received. The [RhCl(COE)(NHC)]$_2$ complexes **1** and **2** (NHC = IPr, IMes, respectively),[15] and RhCl(PPh$_3$)$_3$,[37] were synthesized according to the reported procedures.

NMR spectra were recorded at room temperature (ca. 20 °C) with Bruker AV 300 (300.0 MHz for $^1$H and 75.0 MHz for $^{13}$C{$^1$H}) or Bruker AV 400 (400.0 MHz for $^1$H, 61 MHz for $^2$D, and 100.6 MHz for $^{13}$C{$^1$H}) spectrometers. Shifts are reported relative to external TMS; a residual protonated species in C$_6$D$_6$ ($\delta$ = 7.15 ppm) was used as the internal reference for $^1$H data, with *J* values given in Hz (s = singlet, d = doublet, t = triplet, sept = septet, br. = broad). IR spectra (KBr) were recorded with ATI Mattson Genesis or Bomem–Michelson MB-100 FT-IR spectrometers. Elemental analyses were performed by Mr. M. Lakha of this department on a Carlo Erba EA 1108 analyzer. GC analyses for product yields of the catalytic hydrogenations were performed on a Hewlett–Packard HP 5890, equipped with an FID and an HP-17 capillary column (with pre-column).

**Synthesis of [Rh(H)$_2$Cl(IPr)]$_2$ (3):** A yellow suspension of **1** (64 mg, 0.050 mmol) in hexane (5 mL) was purged with H$_2$, with stirring for 2 h at room temperature, and then the mixture reduced to half the volume under vacuum. The resulting yellowish suspension was refrigerated and then, while cold, filtered through Celite. The collected solid was dried in vacuo at room temperature. Yield 41 mg (74%). C$_{54}$H$_{76}$Cl$_2$N$_4$Rh$_2$·0.5C$_8$H$_{16}$ (1112.42): calcd. C 62.57, H 7.60, N 5.03; found C 62.4, H 7.6, N 4.8. IR: $\tilde{\nu}$ = 2124 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 7.23 (t, *J* = 7 Hz, 2 H, *p*-Ar*H*), 7.07 (d, *J* = 6 Hz, 4 H, *m*-Ar*H*), 6.43 (s, 2 H, NC*H*), 2.92 [sept, *J* = 7 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.34 [d, *J* = 5 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.02 [d, *J* = 5 Hz, 12 H, CH(C*H*$_3$)$_2$], –22.78 (d, *J* = 27 Hz, 2 H, Rh-*H*) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ = 182.7 (d, $J_{\text{Rh-C}}$ = 58 Hz, N*C*N), 147.8 (s, N*C*), 137.5 (s, *i*Pr-*C*), 131.2 (s, *p*-*C*H), 126.6 (s, *m*-*C*H), 124.4 (s, N*C*H), 33.1 [s, *C*H(CH$_3$)$_2$], 27.0 (s, *C*H$_3$), 24.4 (s, *C*H$_3$) ppm.

**[Rh(H)$_2$Cl(IMes)]$_2$ (4):** This complex was prepared in a manner analogous to that described for **3**, but using **2** as the precursor (58 mg, 0.050 mmol). Yield 36 mg (76%). C$_{42}$H$_{52}$Cl$_2$N$_4$Rh$_2$·0.5C$_8$H$_{16}$ (944.23): calcd. C 58.46, H 6.40, N 5.93; found C 58.5, H 6.7, N 6.1. IR: $\tilde{\nu}$ = 2103 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 6.75 (s, 4 H, *m*-Ar*H*), 6.11 (s, 2 H, NC*H*), 2.18 (s, 6 H, *p*-C*H*$_3$), 2.13 (s, 12 H, *o*-C*H*$_3$), –21.61 (br. s, 2 H, Rh-*H*) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ = 138.3 (s, N*C*), 137.7 (s, *p*-Ar*C*), 136.6 (s, *o*-Ar*C*), 129.5 (s, *m*-Ar*C*H), 121.9 (s, N*C*H), 21.8 (s, *C*H$_3$), 19.3 (s, *C*H$_3$) ppm.

**Synthesis of Rh(H)$_2$Cl(IPr)$_2$ (5):** A yellow suspension of **1** (64 mg, 0.050 mmol) and IPr (39 mg, 0.100 mmol) in hexane (10 mL) was purged with H$_2$, with stirring for 2 h at room temperature. The clear yellow solution was then concentrated to one third of the volume; cooling the solution at 0 °C afforded a light yellow crystalline solid that was collected and dried in vacuo. Yield 81 mg (88%). C$_{54}$H$_{74}$ClN$_4$Rh (916.46): calcd. C 70.71, H 8.14, N 6.11; found C 70.6, H 8.3, N 6.2. IR: $\tilde{\nu}$ = 2125 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 7.26 (t, *J* = 7 Hz, 4 H, *p*-Ar*H*), 7.05 (d, *J* = 7 Hz, 8 H, *m*-Ar*H*), 6.44 (s, 4 H, NC*H*), 3.04 [sept, *J* = 7 Hz, 8 H, C*H*(CH$_3$)$_2$], 1.10 [d, *J* = 6 Hz, 24 H, CH(C*H*$_3$)$_2$], 1.00 [d, *J* = 6 Hz, 24 H, CH(C*H*$_3$)$_2$], –22.90 (d, *J* = 33 Hz, 2 H, Rh-*H*) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ = 194.5 (d, $J_{\text{Rh-C}}$ = 36 Hz, N*C*N), 146.8 (s, N*C*), 138.2 (s, *i*Pr-*C*), 129.6 (s, *p*-*C*H), 124.4 (s, *m*-*C*H), 123.9 (s, N*C*H), 28.9 [s, *C*H(CH$_3$)$_2$], 26.3 (s, *C*H$_3$), 23.8 (s, *C*H$_3$) ppm.

**Synthesis of Rh(H)$_2$Cl(IPr)(IMes) (5a):** A yellow suspension of **1** (64 mg, 0.050 mmol) and IMes (30 mg, 0.100 mmol) in hexane (10 mL) was purged with H$_2$, with stirring for 6 h at room temperature. The yellow suspension was then filtered through Celite and the solid obtained was washed with hexane (5 mL) followed by cold Et$_2$O (3 mL). The hexane filtrate was vacuumed to dryness to give **5** in ca. 25% yield, and the collected yellow solid was the known Rh(H)$_2$Cl(IMes)$_2$ (**5′**).[18] The cold ether filtrate was vacuumed to dryness to give a light yellow mixture of **5a** and **5′**. Yield of mixture: 81 mg (25%). Data for **5a**: IR: $\tilde{\nu}$ = 2094 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 7.27 (t, *J* = 7 Hz, 2 H, *p*-Ar*H*-IPr), 7.06 (d, *J* = 7 Hz, 4 H, *m*-Ar*H*-IPr), 6.62 (s, 4 H, *m*-Ar*H*-IMes), 6.54 (s, 2 H, NC*H*-IPr), 6.08 (s, 2 H, NC*H*-IMes), 3.04 [sept, *J* = 7 Hz, 4 H, C*H*(CH$_3$)$_2$], 2.29 (s, 6 H, *p*-C*H*$_3$), 2.11 (s, 12 H, *o*-C*H*$_3$), 1.28 [d, *J* = 7 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.05 [d, *J* = 7 Hz, 12 H, CH(C*H*$_3$)$_2$], –23.21 (d, *J* = 36 Hz, 2 H, Rh-*H*) ppm.

**Synthesis of RhCl(CO)$_2$(IPr) (6):** A yellow suspension of **1** (64 mg, 0.050 mmol) in hexane (5 mL) was purged with CO, with stirring for 1 h at room temperature, and then the mixture was concentrated to half the volume. The precipitated white solid was collected and dried in vacuo. Yield 56 mg (96%). C$_{29}$H$_{36}$ClN$_2$O$_2$Rh (582.15): calcd. C 59.78, H 6.23, N 4.81; found C 60.1, H 6.4, N 4.6. IR: $\tilde{\nu}$ = 2073, 1990 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 7.20 (t, *J* = 7 Hz, 2 H, *p*-Ar*H*), 7.15 (d, *J* = 7 Hz, 4 H, *m*-Ar*H*), 6.63 (s, 2 H, NC*H*), 3.14 [sept, *J* = 7 Hz, 4 H, C*H*(CH$_3$)$_2$], 1.72 (d, *J* = 7 Hz, 12 H, C*H*$_3$), 0.96 (d, *J* = 7 Hz, 12 H, C*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ = 186.0 (d, $J_{\text{Rh-C}}$ = 54 Hz, *C*O ?), 184.2 (d, $J_{\text{Rh-C}}$ = 72 Hz, *C*O), 182.1 (d, $J_{\text{Rh-C}}$ = 45 Hz, N*C*N ?), 146.7 (s, N*C*), 135.9 (s, *i*Pr-*C*), 131.1 (s, *p*-*C*H), 125.3 (s, *m*-*C*H), 124.7 (s, N*C*H), 29.5 [s, *C*H(CH$_3$)$_2$], 26.9 (s, *C*H$_3$), 23.4 (s, *C*H$_3$) ppm.

**Synthesis of RhCl(CO)$_2$(IMes) (7):** This complex was prepared in a manner analogous to that described for **6** but using **2** as precursor (58 mg, 0.050 mmol). Yield 49 mg (98%). C$_{23}$H$_{24}$ClN$_2$O$_2$Rh (498.06): calcd. C 55.42, H 4.86, N 5.62; found C 55.3, H 5.0, N 5.7. IR: $\tilde{\nu}$ = 2070, 1990 cm$^{-1}$. $^1$H NMR (C$_6$D$_6$): $\delta$ = 6.76 (s, 4 H, Ar*H*), 6.13 (s, 2 H, NC*H*), 2.25 (s, 12 H, *o*-C*H*$_3$), 2.05 (s, 6 H, *p*-C*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ = 186.0 (d, $J_{\text{Rh-C}}$ = 54 Hz, *C*O), 179.2 (d, $J_{\text{Rh-C}}$ = 45 Hz, N*C*N), 139.8 (s, N*C*), 136.1 (s, *p*-Ar*C*), 135.9 (s, *o*-Ar*C*), 129.4 (s, *m*-*C*H), 123.7 (s, N*C*H), 23.4 (s, *p*-*C*H$_3$), 19.0 (s, *o*-*C*H$_3$) ppm.

**Synthesis of RhCl(CO)(IPr)$_2$ (8):** This complex was prepared in a manner analogous to that described for **6** but using **5** as precursor

(46 mg, 0.050 mmol). Yield 44 mg (93%). $C_{55}H_{72}ClN_4ORh$ (942.44): calcd. C 70.03, H 7.70, N 5.94; found C 70.1, H 7.4, N 6.1. IR (KBr): $\tilde{\nu}$ = 1938 $cm^{-1}$. $^1H$ NMR ($C_6D_6$): $\delta$ = 7.29 (t, $J$ = 8 Hz, 4 H, *p*-Ar*H*), 7.09 (d, $J$ = 8 Hz, 8 H, *m*-Ar*H*), 6.51 (s, 4 H, NC*H*), 3.14 [sept, $J$ = 7 Hz, 8 H, C*H*($CH_3$)$_2$], 1.14 [d, $J$ = 7 Hz, 24 H, CH(C$H_3$)$_2$], 1.02 [d, $J$ = 7 Hz, 24 H, CH(C$H_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ = 189.8 (d, $J_{\text{Rh-C}}$ = 42 Hz, N*C*N), 188.1 (d, $J_{\text{Rh-C}}$ = 79 Hz, *C*O), 146.9 (s, N*C*), 138.0 (s, *i*Pr-*C*), 131.2 (s, *p*-*C*H), 124.8 (s, *m*-*C*H), 124.5 (s, N*C*H), 29.0 [s, *C*H($CH_3$)$_2$], 26.8 (s, *C*$H_3$), 23.5 (s, *C*$H_3$) ppm.

**Catalytic Hydrogenation:** Inside a glove-box, a benzene solution (10 mL) containing 0.005 mmol of Rh complex and 0.10 mmol of cyclohexene or 1-octene was loaded into a 50 mL Schlenk-tube equipped with a septum and stirrer. The Schlenk was then vacuumed and refilled with 1 atm $H_2$ from a Schlenk-line. The reaction mixture was then stirred, and product formation was monitored by GC; in some cases, the "catalytic solution" was stirred in an oil-bath at 45 °C. With this set-up, even if hydrogenation were complete, the $H_2$ pressure remains essentially constant.

**X-ray Crystallographic Analysis:** Measurements were made at 173.0(1) K on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-$K_\alpha$ radiation (0.71069 Å). Some crystallographic data for **5** are shown in Table 1. Data were collected using the d*TREK software package[38] and processed using TwinSolve,[39] with normalized minimum and maximum transmission coefficients of 0.651 and 0.925, respectively; the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods[40] and expanded using Fourier techniques.[41] The material crystallizes with one half-molecule on a twofold rotation axis, with one isopropyl substituent disordered in two orientations. Additionally, the material crystallizes in the lattice with a 50:50 disordered mixture of hexane and $Et_2O$. Both solvent molecules reside on a twofold rotation axis. All non-hydrogen atoms (except those of the solvents and the disordered isopropyl substituent) were refined anisotropically. All H-atoms were included in calculated positions but not refined. Neither of the Rh-H hydrides could be successfully refined, despite the presence of residual peaks around the Rh; however, two hydrides are clearly seen in the $^1H$ NMR and IR data. The final cycle of full-matrix least-squares refinement on $F^2$ was based on 6022 reflections and 290 variable parameters, and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1 = \Sigma \,||F_o| - |F_c||/\Sigma |F_o|$ = 0.084, and $wR_2 = [\Sigma\, (w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$ = 0.080. The standard deviation of an observation of unit weight was 0.84, the weighting Scheme being based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.69 and –0.63 $e^-/Å^3$, respectively.

Table 1. Crystallographic data for complex **5**.

| Data | **5**·1/2$C_6H_{14}$·1/2($C_2H_5$)$_2$O |
|---|---|
| Formula | $C_{59}H_{86}ClN_4O_{0.5}Rh$ |
| *Fw* | 997.68 |
| Crystal color, habit | yellow, block |
| Crystal size [mm] | 0.25 × 0.20 × 0.20 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12$ (#18) |
| *a* [Å] | 12.952(3) |
| *b* [Å] | 20.569(4) |
| *c* [Å] | 10.599(2) |
| *V* [Å$^3$] | 2824(4) |
| *Z* | 2 |
| $\mu$ [mm$^{-1}$] | 0.389 |
| Total reflections | 29862 |
| Unique reflections | 6022 |
| $R_{\text{int}}$ | 0.052 |
| No. variables | 290 |
| $R1$ [$I > 2\sigma(I)$] | 0.084 (all data) |
| $wR2$[a] | 0.080 (all data) |
| Gof | 0.84 (all data) |

[a] $w = 1/[\sigma^2(F_o^2) + (0.0287\,P)^2 + 0.00\,P]$, where $P = (F_o^2 + 2F_c^2)/3$

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