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Structure and Reactivity of Dinitrogen Rhodium Complexes Containing N-Heterocyclic Carbene Ligands

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The rhodium bis-carbene complex $[Rh(IPr)_2(N_2)Cl]$, where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, has been synthesized and characterized. The complex is a rare example of a four-coordinate rhodium complex featuring nitrogen bound end-on. While quite stable as a solid under inert atmosphere, in solution the N_2 ligand has been found to be quite labile. This lability has been exploited in the synthesis of complexes with the formula $[Rh(IPr)_2(XY)Cl]$, where XY = O_2, H_2 and CO. Interestingly, the dihydride coordination leads to oxidation of the metal centre to Rh^{III}, even though previous studies from our lab have shown that Rh remains in the +1 oxidation state upon coordination of dioxygen.

Introduction

The isolation and characterization of organometallic complexes as intermediates in transition-metal-catalyzed reactions is of great importance to the understanding of catalytic processes. For decades, phosphorus-based ligands have been essential components of late transition-metal catalysts due to the large range of steric and electronic properties they present. However, even these ubiquitous ligands have their limitations: for example, the lability of the phosphorus–metal bond renders them generally unsuitable in the area of oxidation catalysis. In recent years, a new class of ligands has made a dramatic rise in popularity because their properties are generally complementary to commonly employed phosphane ligands: we refer, of course, to N-heterocyclic carbenes (NHCs).

First discovered independently by Öfele[1] and Wanzlick,[2] this class of compounds was studied largely in an organometallic rather than catalytic sense by Lappert and co-workers.[3–6] Isolation of free N-heterocyclic carbenes in the late 80's, early 90's by Bertrand[7] and Arduengo[8] spurred new interest in the field. It was not until several years later, however, that the use of these ligands in place of phosphanes as spectator ligands for metal-catalyzed homogeneous reactions began to be widely examined.[9] These initial reports have been followed by a flurry of activity in the field that has, in recent years, been the subject of numerous reviews[10–14] and books.[15,16]

Our interest in the field has centered on the use of NHC ligands for rhodium and the application of the resulting complexes to homogeneous catalysis.[17] In initial work, direct analogues of Wilkinson's catalyst[18] were prepared in which one of the triarylphosphanes was replaced with either IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-yidene] or SIMes [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene].[19–21] A number of analogues featuring different phosphanes in the overall structure $[Rh(NHC)(PR_3)_2Cl]$ were prepared, and proved to be effective catalysts in both hydrogenation[20] and hydroformylation[19,21,22] reactions. To fully understand the systems involved, we engaged in a study of the thermal and oxidative stability of these complexes.[23] While catalysts of the series $[ClRh(IMes)(PAr_3)(CO)]$ appeared quite oxidatively stable, exposure of $[ClRh(IMes)(PPh_3)_2]$ to oxygen caused formation of a blue complex identified as $[Rh(IMes)(PPh_3)(O_2)Cl]$, which itself displayed limited aerobic stability. Pursuit of full characterization of this type of complex led to the synthesis of bis-NHC analogues $[Rh(IPr)_2(O_2)Cl]$ (**1a**) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and $[Rh(IMes)_2(O_2)Cl]$ (**1b**).[24] These complexes were interesting not only because of their remarkable benchtop stability, but also because of their low-valency (formally square planar at Rh) and short O–O distances compared to most Rh peroxo species. In collaboration with Pierre Kennepohl from the University of British Columbia, we were able to demonstrate that the metal remained unoxidized by coordination of molecular oxygen to rhodium and that the complexes were in fact a rare example of Rh^{I}-O_2-type complexes.

In the present report, we describe our investigation of the coordination of other small molecules to the $Rh(IPr)_2Cl$ framework. Most importantly, in the absence of other ligands, we find that the $Rh(IPr)_2Cl$ framework takes up molecular nitrogen. The solid-state stability of the dinitrogen complex and lability in solution permits it to be used as a surrogate for a number of analogous coordination compounds.

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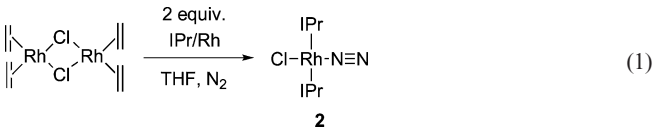
Results and Discussion

Synthesis and Characterization of Complexes [Rh(IPr)$_2$(XY)Cl]

Intrigued by previous findings in which we were able to isolate a rare example of a four-coordinate rhodium-O_2 complex, formally characterized as a Rh^I complex, we investigated the reactivity of the metal centre in the absence of oxygen. The synthesis of **1** is achieved by treating a THF solution of $[Rh(C_2H_4)_2Cl]_2$ with IPr under nitrogen in a glove-box, and then exposing the resulting yellow reaction mixture to air or oxygen. Isolation of this yellow complex prior to oxygen exposure yields a Rh-(η^1-N_2) complex with the formula [Rh(IPr)$_2$(N_2)Cl] (**2**) [Equation (1)]. The compound is isolated by evaporation of the volatiles followed by trituration of the solid with cold hexanes and filtration. X-ray quality crystals of this dinitrogen compound were obtained by slow diffusion of hexane into a concentrated THF solution of **2**, the structure of which is given in Figure 1 along with relevant bond lengths and bond angles.



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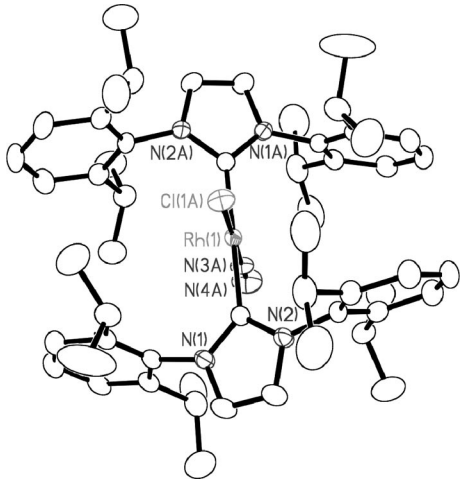


Figure 1. Crystallographically determined structure of [Rh(IPr)$_2$(N_2)Cl] (**2**), displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms are removed for clarity. Selected interatomic distances [Å] and angles [°]: Rh(1)–N(3A), 1.892(7); Rh(1)–C(1), 2.0519(13); Rh(1)–Cl(1A), 2.2882(11); N(3A)–N(4A), 1.100(6); N(1)–C(1), 1.3657(18); N(2)–C(1), 1.3643(18); N(3A)–Rh(1)–C(1), 90.95(4); N(3A)–Rh(1)–C(1)#1, 90.95(4); C(1)–Rh–C(1)#1, 178.10(8); N(3A)–Rh(1)–Cl(1A), 180.0; C(1)–Rh(1)–Cl(1A), 89.05(4); C(1)#1–Rh(1)–Cl(1A), 89.05(4).

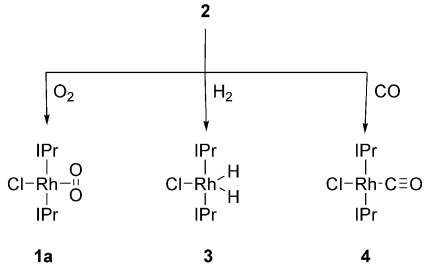
The N–N bond of bound nitrogen in **2** has a bond length of 1.100(6) vs. 1.0975 Å in free nitrogen,[25] and the ν(N–N) appears in the IR at 2103 cm^{-1}. Binding of N_2 to rhodium appears to have caused only a slight lengthening of its interatomic distance, a phenomenon also observed upon binding of dioxygen in complex **1**, likely resulting from poor overlap of d_{xz} and d_{xy} orbitals on Rh with available π^* orbitals of the dinitrogen ligand. The very slight elongation of the N–N bond seems to contradict the relatively strong π back-donation indicated by the vibrational spectra relative to an analogous compound in the literature. Stephan et al. isolated the compound {CH[C(Me)(N*i*Pr$_2$C$_6$H$_3$)]$_2$-Rh(N_2)(COE)}, which has a nearly identical bond length (1.091 Å) and yet a wave number of 2175 cm^{-1}, indicating weaker back-donation.[26] It has been pointed out in the above report (and appears to be the concensus throughout the literature) that no correlation exists between the bond length observed by X-ray analysis and the strength of this bond indicated by IR. It is generally accepted, however, that the qualitative information obtained from the vibrational spectra is more accurate.[27]

As with **1**, four-coordinate square-planar rhodium complexes of molecular nitrogen bound end-on are quite rare, and typically involve ancillary ligands which are bulky and electron-rich. Some of these previously reported structures are analogous to the one which we report here, having the general formula *trans*-[L$_2$Rh(N_2)X] (X = halogen or hydrogen), where in our case L is the NHC IPr. When L = P*i*Pr$_3$[28,29] or PCy$_3$[30,31] and X = Cl, the reported structures have nearly identical ν(N–N) stretches to those found in this investigation (2100 and 2103 cm^{-1}, respectively). In the case of the P*i*Pr$_3$ complex, the Rh–N and N–N bond lengths [1.885(4) and 0.958(5)] are similarly reasonably close to those observed by us for compound **2**.[29] Milstein's group has reported a series of four-coordinate Rh–N_2 complexes featuring trivalent PCP ligands with ν(N–N) stretches ranging from 2110 to 2165 cm^{-1}.[32–34] One other example of a low-valent rhodium complex of molecular nitrogen was reported by Caulton's group featuring a unique PNP ligand, [(*t*Bu$_2$PCH$_2$SiMe$_2$)$_2$N]Rh(N_2), which has a very low ν(N–N) of 2068 cm^{-1}.[35] Interestingly, the three-coordinate fragment of Caulton's complex[36] and the similar (PCP)-Rh complex, [Me$_2$C$_6$H(CH$_2$P*t*Bu$_2$)$_2$]Rh, reported by Milstein[37] coordinate oxygen to give Rh^I–O_2 complexes similar to **1a** and **1b** with O–O bond lengths of 1.363 and 1.365 Å, respectively.

Compound **2** exhibits reasonable stability in the solid state and can be kept under nitrogen for extended periods of time without noticeable degradation. Furthermore, it has been previously shown that through introduction of other molecules, such as dioxygen, access to different coordination complexes are possible via complex **2**. In this way, **2** may act as a surrogate for the yet unreported coordinatively unsaturated [Rh(IPr)$_2$Cl], which is also observed for analogous compounds such as [Rh(P*i*Pr$_3$)$_2$(N_2)Cl] and [Rh(PCy$_3$)$_2$-(N_2)Cl].

With this in mind, we treated **2** independently with both H_2 and CO gases. Nolan and co-workers have previously shown that treating a solution of [Rh(COE)$_2$Cl]$_2$ and two equivalents of IMes in THF with CO or H_2 gave complexes of the formula [Rh(IMes)$_2$Cl(XY)].[38] Analogously, reaction of **2** with CO or H_2 gave [Rh(IPr)$_2$(H)$_2$Cl] (**3**) and [Rh(IPr)$_2$(CO)Cl] (**4**), respectively (Scheme 1). Preparation of the two complexes is carried out similarly to the prepara-

tion of **1**: a THF solution of **2** (from a previously prepared sample or one prepared in situ) is degassed to remove the nitrogen which is then refilled with carbon monoxide or hydrogen. In the case of the carbon monoxide complex **4**, purification can be performed under aerobic conditions as no further reactivity is observed. However, the dihydride appears to be oxidatively sensitive and upon exposure to oxygen reacts to form dioxygen complex **1a**, necessitating anaerobic purification of **3**. Personal communication with B. R. James[39] indicates that a similar reaction was also observed in his laboratories.



Scheme 1. Synthesis of bis-IPr rhodium complexes featuring various diatomic ligands.

X-ray quality crystals of both **3** and **4** were obtained by diffusion of hexane into concentrated THF solutions of the corresponding compounds, and are shown along with relevant bond lengths and bond angles in Figures 2 and 3, respectively (crystallographic parameters of **2**–**4** are presented in Table 1). The structural parameters of these three compounds possess a number of similarities as would be expected because their overall structure does not change significantly.

All three of these structures are pseudo-square planar with slight distortions arising from a subtle tilting of the two rhodium–carbene bonds towards the chloro ligand. For each of these three compounds, as well as **1**, there is a dihedral angle of about 70° between the heterocyclic rings of the *trans* carbene ligands which minimizes steric interactions between the IPr ligands themselves and the *cis* chloro and (XY) ligands. The rhodium–carbene bonds are nearly identical for **2** and **4**, but slightly shorter in the case of **3**, a feature attributable to the difference in oxidation states between the former compounds which are Rh^{I}, and the latter, which is formally Rh^{III}. Spectroscopically, however, no difference in this bonding can be detected, as for all three compounds the $J_{Rh\text{-}C}$ of the carbene signal in the ^{13}C NMR spectra is ca. 40 Hz.

The crystal packing of each structure is dictated almost entirely by the large carbene ligands positioned *trans* to one another, further exacerbating these similarities and causing positional disorder around the Cl–Rh–(XY) nucleus of the molecule. As is commonly noted in related complexes, the relative orientation of the Cl and XY groups within the crystal appears to be arbitrary with a nearly statistical distribution of groups in either direction. The disorder observed in this area leads to uncertainty in the X–Y bond lengths of these structures, which complicated the analysis

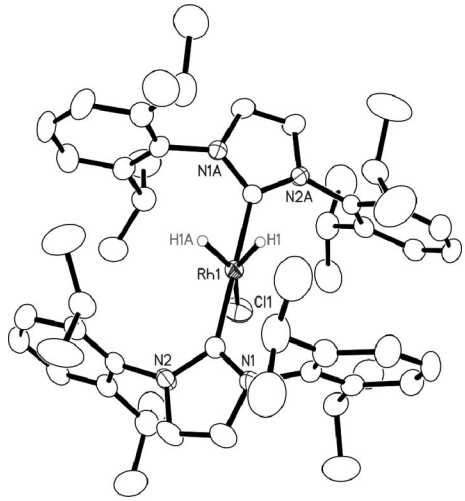


Figure 2. Crystallographically determined structure of the major component in the synthesis of $Rh(IPr)_2(H)_2Cl$ (**3**), displaying thermal ellipsoids drawn at the 50% confidence level. Selected interatomic distances [Å] and angles [°]: Rh(1)–H(1), 1.68(4); Rh(1)–C(1), 2.038(3); Rh(1)–Cl(1), 2.3628(12); N(1)–C(1), 1.372(4); H(1)–Rh(1)–Cl(1), 156.8(15); H(1)–Rh(1)–H(1A), 46.3(30); C(1)–Rh(1)–Cl(1), 90.91(8); C(1)#1–Rh(1)–Cl(1), 90.91(8); C(1)–Rh(1)–H(1), 93.0(18); C(1)#1–Rh(1)–H(1), 85.3(18); C(1)–Rh(1)–C(1)#1, 178.18(17).

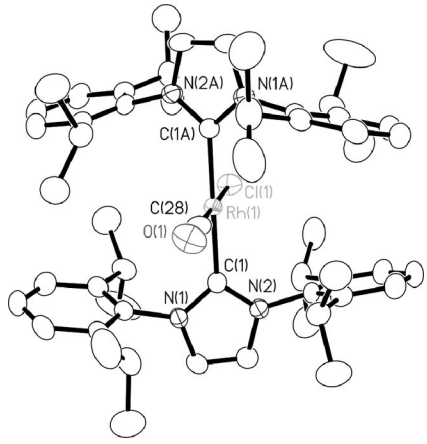


Figure 3. Crystallographically determined structure of $[Rh(IPr)_2(CO)Cl]$ (**4**), displaying thermal ellipsoids drawn at the 50% confidence level. Selected interatomic distances [Å] and angles [°]: Rh(1)–C(28), 1.839(11); Rh(1)–C(1), 2.0555(15); Rh(1)–Cl(1), 2.313(3); C(28)–O(1), 1.156(13); C(28)–Rh(1)–C(1), 90.66(4); C(28)–Rh(1)–Cl(1), 180.0; C(1)–Rh(1)–Cl(1), 89.34(4); C(1)#1–Rh(1)–C(1), 178.69(9).

of the bonding mode in **1**, and may explain the considerably short N–N bond (1.100 Å) observed for **2**. For this reason, it is essential to examine other characteristics of the molecule to obtain information about bonding, such as vibrational spectroscopy or X-ray absorption spectroscopy.

The crystal structure of dihydride **3** is characterized again by a *trans* relationship between the two carbene ligands, with the chloro and hydride ligands occupying the basal plane in this formally trigonal-bipyrimidal structure, similar to that observed by Nolan et al.[38] Hydride ligands were observed crystallographically and have bond lengths of

Table 1. Crystallographic data for compounds **2**, **3/5**, and **4**.

Complex	**2**	**3/5**	**4**
Formula	$C_{60}H_{86}ClN_6Rh$	$C_{60}H_{87.21}Cl_{1.39}N_4Rh$	$C_{61}H_{86}N_4ClORh$
Fw	1029.74	1016.91	1029.70
Crystal dimensions [mm^3]	$0.35 \times 0.30 \times 0.25$	$0.30 \times 0.25 \times 0.20$	$0.45 \times 0.30 \times 0.20$
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*P*2(1)2(1)2	*P*2(1)2(1)2	*P*2(1)2(1)2
a [Å]	13.0317(6)	13.00230(10)	13.0505(10)
b [Å]	20.6605(9)	20.6116(3)	20.6813(16)
c [Å]	10.6499(5)	10.63610(10)	10.6549(9)
V [Å^3]	2867.4(2)	2850.46(5)	2877.0(4)
Z	2	2	2
T [K]	180(2)	180(2)	180(2)
$D_{calcd.}$ [g cm^{-3}]	1.196	1.184	1.189
μ [mm^{-1}]	0.386	0.405	0.385
F(000)	1106	1086	1100
θ range [°]	2.15–28.28	1.85–26.00	1.91–25.00
Index ranges (*h*,*k*,*l*)	±16, ±26, ±14	–16–14, –19–25, ±13	±15, ±24, ±12
No. of reflections collected	31416	14522	16993
No. of independent reflections / R_{int}	6676 / 0.0234	5600 / 0.0304	5073 / 0.0218
No. data / restraints / parameters	6676 / 0 / 297	5600 / 3 / 323	5073 / 0 / 306
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0227 / 0.0584	0.0373 / 0.0954	0.0210 / 0.0504
R_1 / wR_2 (all data)	0.0243 / 0.0590	0.0463 / 0.1003	0.0272 / 0.0688
GOF (on F^2)	1.053	1.055	1.017
Largest diff. peak/hole [e Å^{-3}]	0.352 / –0.311	0.653 / –0.438	0.279 / –0.139

1.68(4) Å, again consistent with the related Nolan complex prepared by an alternate route.

We were particularly interested in understanding the bonding in complex **3**, as we have previously shown that addition of oxygen to the $Rh(IPr)_2Cl$ fragment *does not result in oxidation of the metal centre*. Both XAFS and DFT studies suggest that rhodium maintains a +1 oxidation state upon binding of O_2. For this reason, it was important to distinguish between classical dihydride [Rh^{III}-$(H)_2$] and non-classical dihydride[Rh^{I}-(H_2)] structures for complex **3**. This can be conveniently done by measuring the relaxation time of the hydride signal in the ^{1}H NMR.[40,41] Determination of the T_1 time of the hydride signal in ^{1}H NMR by the typical method gave a value of 282 ms, indicative of a classical metal hydride. This leads to the interesting conclusion that hydrogen gas is able to oxidize the metal centre of $Rh(IPr)_2Cl$, while oxygen is not.

Interestingly, the crystal structure of **3** also appears to contain the structure $Rh(IPr)_2Cl_2$ (**5**) in a relatively large abundance (about 39%) (Figure 4). This was somewhat surprising considering the very sharp NMR spectra of the bulk material, with no obvious indication of the presence of any paramagnetic material. However, closely related paramagnetic impurities have been observed and characterized in complexes derived from Wilkinson's complex[18,42,43] and appear to result from incomplete reduction of rhodium in the synthesis of starting materials. To verify the amount of **5** in the bulk sample of **4**, EPR spectra were obtained confirming that a paramagnetic species was present in relatively low abundance within the sample. Considering the weakness of the EPR signal in the bulk material, it is likely that the small amounts of **5** present in bulk **3** crystallized preferentially along with the structurally similar **3**.

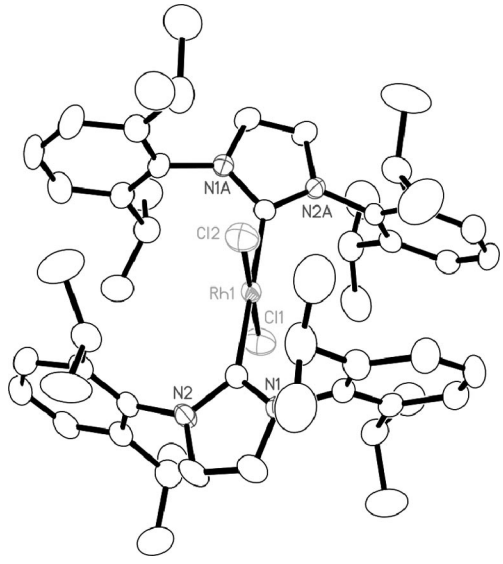
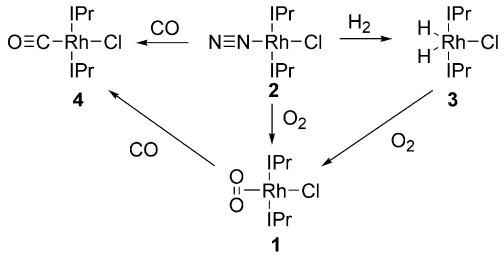


Figure 4. Crystallographically determined structure of the paramagnetic impurity [$Rh(IPr)_2Cl_2$ (**5**)] in the synthesis of compound **3**, displaying thermal ellipsoids drawn at the 50% confidence level.

Relative Stability

Through the study of compounds **1**–**4**, we have been able to gain an understanding of the relative stabilities of these complexes. Dinitrogen complex **2** can be used as a precursor to all other compounds described herein, which is an indication of the lability of this ligand with respect to the other ligands tested. Dioxygen complex **1** can also be prepared from **3**, however oxidation of the carbon monoxide complex **4** did not lead to dioxygen compound **1**. Remarkably, **4** has such high oxidative stability that even after refluxing a tolu-

ene solution of **4** in air for 24 h, no formation of **1** was observed. Since Milstein has reported Rh–O_2 complexes in which N_2 can be used to displace oxygen,[37] we have attempted to prepare **2** from **1** by refluxing a toluene solution of the oxygen adduct under a nitrogen, but with no noticeable production of the nitrogen adduct (Scheme 2).



Scheme 2. Relative reactivity of the [Rh(IPr)$_2$Cl(XY)] compounds.

It therefore appears, that as one might expect, the carbon monoxide adduct is the most stable, while nitrogen is the most reactive. From this study a trend of stability for this series of complexes can be stated as follows:

Rh–N_2 < Rh–$(H)_2$ < Rh–O_2 < Rh–CO

A similar series of stabilities has been previously proposed for molecules of the formula [ClRh(P*i*Pr$_3$)$_2$(XY)], however, the oxygen complex was expectedly less stable in this series, likely due to the presence of oxidatively sensitive phosphane ligands.[28]

Conclusions

We have prepared a series of complexes of the type [ClRh(IPr)$_2$(XY)], where XY is O_2, N_2, H_2 and CO. Characterization of these complexes shows striking similarity in both their X-ray crystal structures as well as their NMR spectra. Interestingly, from the N_2 complex, **2**, the other three complexes can be easily prepared suggesting that **2** may acting as a surrogate for the coordinatively unsaturated three-coordinate complex [ClRh(IPr)$_2$]. Access of this proposed intermediate may lead to exciting future discoveries in coordination chemistry, as well as catalytic chemistry where precoordination of the substrate is required.

Experimental Section

General Considerations: All manipulations were carried out under nitrogen in a glovebox or using standard Schlenk techniques. THF, toluene and hexane were purified with a PureSolv Solvent Purification system, degassed by at least three freeze-pump-thaw cycles and stored over 4-Å molecular sieves prior to use. Deuterated solvents were distilled from CaH_2, degassed by at least three freeze-pump-thaw cycles and stored over 4-Å molecular sieves prior to use. [Rh(C$_2$H$_4$)$_2$Cl]$_2$[44] and IPr[45] were prepared according to previously reported literature procedures. H_2, CO, and N_2 gases were purchased from Praxair and used without purification. ^{1}H NMR spectra were recorded with a 400- or 500-MHz spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using residual protonated solvent as an internal standard (C_6D_6, 7.15 ppm. CD_2Cl_2, 5.32 ppm). ^{13}C NMR spectra were recorded with a 100- or 125-MHz spectrometer. Chemical shifts are reported as above using the solvent as an internal standard (C_6D_6, 128.0 ppm. CD_2Cl_2, 53.8 ppm). Elemental analyses were performed by Canadian Microanalytical Systems Ltd. X-ray data collection was performed with a Bruker SMART CCD 1000 X-ray diffractometer.[46]

[Rh(IPr)$_2$(N$_2$)Cl] (2): A 25 mL Schlenk flask was charged with [Rh(C$_2$H$_4$)Cl]$_2$ (51.3 mg, 0.132 mmol) and IPr (206.7 mg, 0.532 mmol), and the solids dissolved in THF (10 mL). The resulting yellow solution was stirred for 4 h and then the volatiles were removed in vacuo. The yellow residue was then triturated with cold hexane and collected by filtration. X-ray quality crystals were obtained by slow diffusion of hexane into a concentrated THF solution of the product. Yield 103 mg (41%). $C_{54}H_{72}ClN_4Rh\cdot0.75H_2O$ (929.06): calcd. C 69.81, H 7.97, N 6.03; found C 70.16, H 8.19, N 5.63. IR (KBr): $\tilde{\nu}$ = 2103 (N–N, s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.31 (t, J = 8 Hz, 4 H), 7.10 (d, J = 8 Hz, 8 H), 6.62 (s, 4 H), 3.14–2.54 (m, 8 H), 0.98–0.79 (m, 48 H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ = 191.1 (d, $J_{Rh\text{-}C}$ = 40 Hz), 147.9, 145.3, 137.9, 128.7, 123.9, 28.4, 25.8, 22.6 ppm.

[Rh(IPr)$_2$(H)$_2$Cl] (3): A 25 mL Schlenk flask was charged with [Rh(C$_2$H$_4$)Cl]$_2$ (51.0 mg, 0.131 mmol) and IPr (207.5 mg, 0.534 mmol), and the solids dissolved in THF (10 mL). The solution was frozen with liquid nitrogen, the atmosphere removed by vacuum and the flask charged with hydrogen gas. The reaction was stirred at room temperature for 16 h and then the solvent was removed in vacuo to give a light brown solid. The residue was triturated with cold hexane and collected by filtration. X-ray quality crystals were obtained by slow diffusion of hexane into a concentrated THF solution of the product. Yield 130.1 mg (54%). $C_{54}H_{74}ClN_4Rh\cdot1H_2O$ (939.59): calcd. C 69.33, H 8.19, N 5.99; found C 69.14, H 7.94, N 5.89. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.31 (t, J = 8 Hz, 4 H), 7.03 (d, J = 8 Hz, 8 H), 6.75 (s, 4 H), 2.72 (m, 8 H), 0.91 (m, 48 H), –23.51 (d, $J_{Rh\text{-}H}$ = 35 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ = 193.7 (d, $J_{Rh\text{-}C}$ = 41 Hz), 146.4, 137.6, 129.2, 124.0, 123.8, 28.4, 25.7, 23.1 ppm.

[Rh(IPr)$_2$(CO)Cl] (4): A 25 mL Schlenk flask was charged with [Rh(C$_2$H$_4$)Cl]$_2$ (19.2 mg, 0.0494 mmol) and IPr (76.7 mg, 0.197 mmol), and the solids dissolved in THF (10 mL). The resulting yellow reaction mixture was stirred in the glovebox under nitrogen and then removed to the Schlenk line, degassed and purged with CO. An immediate colour change to a colourless reaction mixture is observed, signalling formation of **4**. The volatiles are then removed and the resulting beige solid is triturated with cold hexane and collected by filtration. X-ray quality crystals were obtained by slow diffusion of hexane into a concentrated THF solution of the product. $C_{55}H_{72}ClN_4ORh\cdot2H_2O$ (979.59): calcd. C 67.44, H 7.82, N 5.72; found C 66.40, H 7.37, N 5.44. IR (KBr): $\tilde{\nu}$ = 1940 (C–O, s) cm^{-1}. ^{1}H NMR ([D$_8$]toluene, 400 MHz): δ = 7.26 (t, J = 8 Hz, 4 H), 7.05 (d, J = 8 Hz, 8 H), 6.50 (s, 4 H), 3.06 (br., 8 H), 1.04 (m, 48 H) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 100 MHz): δ = 189.4 (d, $J_{Rh\text{-}C}$ = 42 Hz), 187.5 (d, $J_{Rh\text{-}C}$ = 80 Hz), 146.5, 137.8, 129.4, 124.2, 124.0, 28.7, 26.4, 23.1 ppm.

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