FULL PAPER

# A simple synthetic route to [Rh(acac)(CO)(NHC)] complexes: ligand property diagnostic tools and pre-catalysts

Sébastien G. Guillet,[a] Gianmarco Pisanò,[a] Soumyadeep Chakrabortty,[b] Bernd H. Müller,[b] Johannes G. de Vries,[b] Paul C. J. Kamer,[b]† Catherine S. J. Cazin[a] and Steven. P. Nolan*[a]

**Abstract:** An operationally simple, user and eco-friendly synthetic protocol for the synthesis of [Rh(acac)(CO)(NHC)] complexes is described. Insights into the mechanism are provided using operando spectroscopy. The spectroscopic fingerprints of these complexes are correlated to NHCs reported electron-donating descriptor values, highlighting a new strategy to evaluate carbenes' electronic properties. An assessment of these complexes in catalytic applications is also reported, showing promising results in the catalytic hydrogenation of aromatic ketones.

## Introduction

During the past two decades, N-heterocyclic carbenes (NHC) -transition metal complexes have attracted tremendous interest across various fields ranging from catalysis,[1] polymers[2] to materials science.[3] Having gained the status of *privileged ligand* in numerous catalytic transformations,[4] a better understanding of ligand effects has been made possible through the advent of descriptors that quantify the NHC steric and electronic properties. Two main NHC parameters have emerged as indicators of the potential of the ligand. The first, one determining the steric contribution to M-L bonding and hindrance around the metal, is usually measured through the percent buried volume descriptor.[5] As for electronic properties, a plethora of methods have been developed to estimate the donor properties of ligands.

One noteworthy method, developed by Tolman, makes use of the infrared carbonyl stretching frequencies of $[Ni(CO)_3L]$ complexes characterizing any given L when the tricarbonyl complex is accessible.[6] This Tolman Electronic Parameter (TEP) is still used to date as a reference metric for electronic donation characterising any given L (Figure 1). However, the toxicity of $Ni(CO)_4$ has encouraged researchers to turn to other systems or methods to determine these TEP values.[7,8] Some of these methods, also using the IR data of the carbonyl region, focus on $[MCl(CO)_2L]$ type complexes (where L is the ligand to analyse and M = Rh[9,10] or Ir[11,12]). A drawback to these systems is the multistep method required for their synthesis. The electronics of a ligand can also be evaluated *via* the redox potential of complexes bearing the desired ligand (these electronic values are referred to as Lever's electronic parameter or LEP).[9-13] More recent methods have also made use of NMR to obtain electronic property information, yet using this approach, it must be kept in mind that local environments (other ligands) also influence these values, whereas analysis of infrared data remains simpler.[8] Amongst these NMR methods, some exploit the $^{13}C$ shift of the C2 carbon of the imidazole ring in organometallic complexes (Huynh's electronic parameter, HEP),[14] other rely on the presence of heteroatoms via $^{31}P$ or $^{77}Se$ NMR in carbene-phosphidiene[15] or selenoureas[16] compounds, respectively. More recently work has been carried out to establish a relation between electronic parameters of a NHC and the $J_{CH}$ coupling constant of the corresponding imidazolium salt.[17]

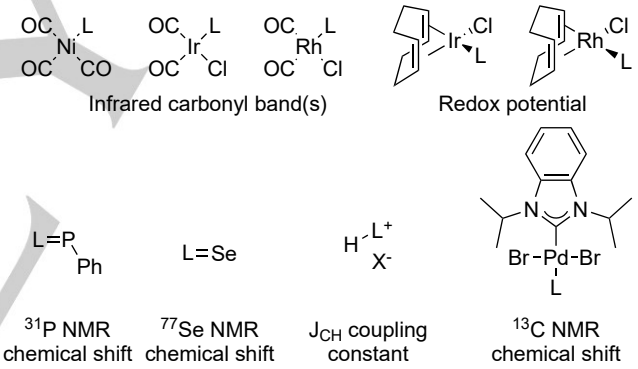



Figure 1. Reported methods and compounds for electronic parameter evaluation of phosphines and NHCs ligands (in all structures, L is the ligand whose electronic properties are evaluated).[8]

More recently, Carrow *et al.* have demonstrated that a linear correlation could be established between the TEP and the stretching frequencies of any other metal-NHC complexes family[18], using a correlation approach previously employed for Ir and Rh systems. The excellent linear correlation between the TEP and the infrared carbonyl band of $[Rh(acac)(CO)(PR_3)]$ for phosphine ligands was highlighted.[18] One significant advantage of this system is its ease of access for phosphine derivatives as their synthesis simply involves a CO displacement by an incoming ligand L in $[Rh(acac)(CO)_2]$. These complexes are easily prepared in a one-step reaction, and are air stable, making them excellent tools for electronic parameter evaluation. Although Carrow *et al.* excluded NHCs from their work because these did not fit their determined linear correlation, it is possible that this group follows a different correlation, and the two examples studied by Carrow *et al.* are insufficient to determine whether this is indeed the case. A wider range of [Rh(acac)(CO)(NHC)] complexes would allow to

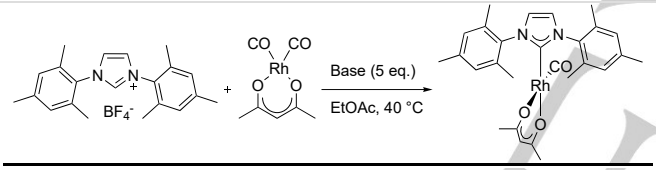
[a] S. G. Guillet, G. Pisanò, Prof. Dr. C.S.J. Cazin, Prof. Dr. S. P. Nolan
Department of Chemistry and Centre for Sustainable Chemistry
Ghent University
Campus Sterre, Building S-3
Krijgslaan 281, 9000 Ghent, Belgium
E-mail: steven.nolan@ugent.be
[b] https://nolan.ugent.be
[c] S. Chakrabortty, Prof. Dr. P.C.J. Kamer, Prof. Dr. J.G. de Vries and Dr. B. H. Müller
Leibniz-Institut für Katalyse e.V. (LIKAT Rostock)
Albert-Einstein-Str. 29a, 18059 Rostock, Germany
† Deceased on 19-11-2020.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

determine if such a relation exists, and if so, it would provide an easy and non-toxic access to the electronic parameter of all NHCs via this simple synthetic method. Although the phosphine analogues are well known,[18,19] the NHC congeners have been almost completely overlooked. Only a limited number reports on their synthesis exist, always involving the use of a free carbene and not focusing on any catalysis.[20] We suspect this difficult access has hampered the exploration of catalytic uses of these complexes. We reasoned that their synthesis could be achieved through the *weak base approach* we have deployed during the past few years.[21,22]

## Results and Discussion

To assess the possibility to prepare [Rh(acac)(CO)(NHC)] complexes through a weak base approach, the reaction between NHC•$HBF_4$ salts and [Rh(acac)$(CO)_2$] was investigated with different weak bases. The reactions were monitored via *in situ* FT-IR spectroscopy. Satisfyingly, when IMes•$HBF_4$ (IMes = *N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene) was used in this substitution reaction, all three bases tested ($K_2CO_3$, $NEt_3$ and NaOAc) permitted formation of the desired [Rh(acac)(CO)(IMes)] complex (Table 1). Since the procedure was more straightforward and the reaction faster with triethylamine, this base was selected for further investigations.

Table 1. Base screening for the formation of [Rh(acac)(CO)(IMes)].

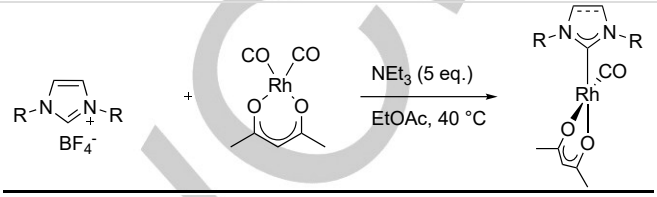



| Entry | Base | Time (h) | Isolated yield (%) |
|---|---|---|---|
| 1 | $K_2CO_3$ | 8 | 79 |
| **2** | **$NEt_3$** | **3** | **96** |
| 3 | NaOAc | 18 | 74 |

Reaction conditions: [Rh(acac)$(CO)_2$] (0.4 mmol), IMes•$HBF_4$ (0.4mmol), base (2 mmol) in EtOAc (4 mL) at 40 °C until *in situ* monitoring shows complete disappearance of rhodium precursor.

To explore whether the method was at all versatile, various NHC•$HBF_4$ were then investigated. If IMes and IPr (IPr = N,N'-bis[2,6-(diisopropyl)phenyl]imidazol-2-ylidene) complexes could be easily prepared at room temperature, SIMes (SIMes = *N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazolidin-2-ylidene) and the bulkier IPr* (IPr* = *N,N'*-bis (2,6-bis(diphenylmethyl)-4-methylphenyl) imidazolidin-2-ylidene) required slight heating in order to afford good yields. Moreover, *in situ* FT-IR monitoring showed that even at 40 °C, a temperature where every NHC•$HBF_4$ was able to react, the rate of the reaction was NHC dependent: IMes being very fast when SIMes took a much longer time to reach completion. To our surprise, SIPr•$HBF_4$ (SIPr = *N,N'*-bis[2,6-(di-isopropyl)phenyl]imidazol-2-ylidene) was unable to react under these conditions and a temperature of 60 °C was needed. At this temperature conversion was slow and decomposition became competitive. Luckily, the same procedure with $K_2CO_3$ allowed access to the Rh-SIPr complex without any decomposition. Additionally, alkyl substituted NHCs such as ICy (ICy = *N,N'*-bis(cyclohexyl)imidazol-2-ylidene) did not lead to any product formation (Table 2), the reasons behind this failure are presently being studying. The synthesis of the complexes using the weak base route was also performed under solvent-free conditions using a ball mill. Satisfyingly, all Rh-NHC complexes could be prepared efficiently in this manner.

Table 2. The scope of compatible NHC•$HBF_4$ precursors.




| Entry | Product | NHC•$HBF_4$ | Time (h) | Isolated Yield (%) |
|---|---|---|---|---|
| 1 | **Cat-1** | IMes | 3 | 96 |
| 2 | **Cat-2** | IPr | 5 | 85 |
| 3 | **Cat-3** | IPr* | 18 | >99 |
| 4 | **Cat-4** | SIMes | 6 | 97 |
| 5[a] | **Cat-5** | SIPr | 4 | >99 |
| 6 | **Cat-6** | ICy | 24 | - |

All reactions were conducted until FT-IR *in situ* monitoring showed complete disappearance of the [Rh(acac)$(CO)_2$] precursor. Reaction conditions: [Rh(acac)$(CO)_2$] (0.4 mmol), NHC•$HBF_4$ (0.4 mmol), $NEt_3$ (2 mmol) in EtOAc (4 mL) at 40 °C. (a) Reaction conditions: $K_2CO_3$ (5 equiv), 60 °C.

Having demonstrated the versatility and efficiency of this method, the next element to examinate was the mechanism of this reaction. During the FT-IR monitoring, no intermediate was observed on the IR time scale. To gather more information on the inner workings of this reaction, a kinetic study was conducted on the reaction involving IMes•$HBF_4$ and [Rh(acac)$(CO)_2$]. First, a reaction was conducted with excess base (5 equivalents) and NHC•$HBF_4$ (3 equivalents) to examine the role of the rhodium precursor. The FT-IR monitoring revealed that the rate of disappearance of [Rh(acac)$(CO)_2$] follows first order kinetics (Supporting information, Figure S1). Monitoring the reaction with a stoichiometric amount of metal precursor and NHC•$HBF_4$ clearly indicated the same exponential decrease of the amount of the rhodium reactant, which supports a kinetic expression ruling out any NHC•$HBF_4$ concentration-dependant term (Supporting information, Figure S2). This proves that the carbene precursor is either absent of the rate determining step, or that this step starts from an intermediate containing both the NHC and the rhodium moiety.

To account for the base concentration included in the determined pseudo constant and to highlight the role of the base in the rate of the reaction, reaction kinetics were monitored where varied amounts of triethylamine were used. These reactions clearly indicate that the base has a first order contribution to the rate expression (Figure 2, graph a). With these elements in hand, the kinetic rate expression was established as rate =

k(T)[Rh][$NEt_3$], where k(T) is the kinetic rate constant, and [Rh] and [$NEt_3$] are the respective concentration in these two reactants.

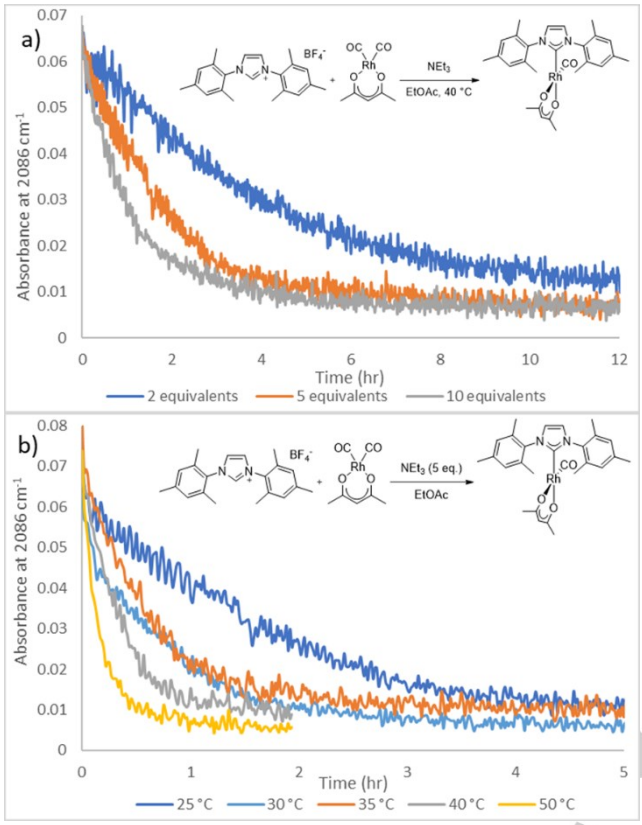



Figure 2. Effect of base concentration (a) and temperature (b) on reaction rate. Conditions: [Rh(acac)$(CO)_2$] (100 mg, 0.39 mmol), IMes·$HBF_4$ (0.39 mmol, 1 eq.), $NEt_3$ in EtOAc (4 mL).

Reaction kinetics were monitored as a function of temperature, (Figure 2, graph b) permitting the determination of activation parameters. The Eyring plot (Supporting information, Figure S3) permits the determination of activation enthalpy and entropy values of $\Delta H^{\dagger}$ = 17.1 kcal.mol$^{-1}$ and $\Delta S^{\dagger}$ = -17.8 cal.mol$^{-1}$K$^{-1}$. The clearly large negative value of the activation entropy suggests an ordered transition state and supports a concerted reaction mechanism for the formation of [Rh(acac)(CO)(NHC)] complexes. This is consistent with the most commonly adopted mechanism for weak base assisted synthesis of metal-NHC complexes.[21]

We next examined a possible correlation between the carbonyl stretching frequency of our rhodium complexes bearing NHC ligands and the traditional Tolman electronic parameter as was explored by Carrow *et al.* for rhodium phosphine complexes.[16] Although five complexes offer a limited dataset to establish such a correlation, it is evident that there is already a proportionality between the two values (see Figure 3, exact values can be found in the supporting information). Work aimed at expanding the dataset is ongoing in our laboratories and the approach creates a simple method to easily measure/quantify the donor properties of NHC ligands.

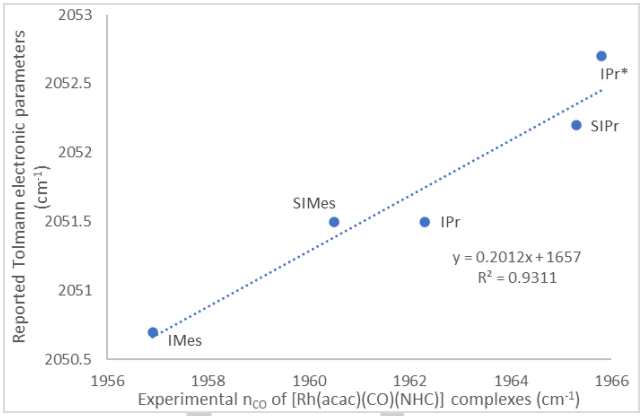


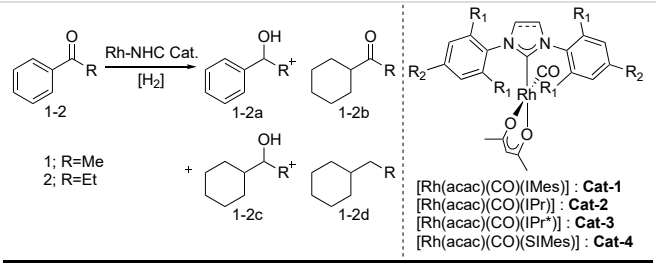

Figure 3. Linear correlation between the IR carbonyl band of [Rh(acac)(CO)(NHC)] complexes and literature reported TEP[18]

Having simple access to these complexes, we next examined their possible catalytic activity. Selective addition of dihydrogen to carbon-carbon or carbon-heteroatom double bonds is one of the most powerful methods that provides access to numerous saturated motifs and is applied frequently in the production of fine chemicals.[23] The use of the combination of transition metals with phosphines, as structurally defined metal-phosphine complexes, is the most general approach for homogeneous hydrogenation. However, recently, the application of transition metal-carbene complexes as hydrogenation catalysts has emerged as quite promising.[24] Recently, the [RhCl(CAAC)(COD)] (CAAC = cyclic (alkyl)(amino)carbene, COD = cyclooctadiene) complex has been used for the chemoselective hydrogenation of fluoroarenes and fluoropyridine by Glorius and co-workers.[25] In addition, Bullock and co-workers showed that cyclohexyl-silanes and borylated cyclohexanes could also be readily prepared from their corresponding silyl arenes and aryl boronic esters using the same Rh-CAAC catalytic system.[26,27]

However, selective hydrogenation of aryl ketones using these Rh-NHC catalysts has thus far scarcely been studied. In fact, selectivity-control in this hydrogenation process represents a key challenge. Recently, Leitner and co-workers have reported on a triphenylphosphonium-based immobilized Rh@SILP system able to catalyse the chemoselective hydrogenation of aromatic ketones to saturated alcohols or to hydrodeoxygenated alkanes, as a function of thermal conditions.[28] In 2015, Zeng and co-workers described a Rh-CAAC system effective in producing saturated ketones via hydrogenation of aryl ketones and phenols.[29] Interestingly, very low conversions of the aryl ketones into the hydrogenated products were observed using the *in situ* formed Rh-NHC (IMes and IPr) complexes.

In contrast to the [Rh(COD)Cl(NHC)] catalysts,[29] a relatively high conversion was observed in the hydrogenation of acetophenone in trifluoroethanol (TFE) at 80°C using 1 mol% of [Rh(acac)(CO(NHC)] catalyst. A similar product distribution was observed using **cat-2** or **cat-4** (Table 3, entries 1 and 2), with a high selectivity towards the saturated alcohol (**1c**). The reactions were also performed for longer periods (48 hrs.) in order to examine whether the conversion of **1b** into **1c** was time dependent.

Table 3. Rh-NHC catalysed selective hydrogenation of aryl ketone.




| Entry[a] | Substrate | Rh-NHC cat | a[d] | b[d] | c[d] |
|---|---|---|---|---|---|
| 1[a] | 1 | **Cat-2** | - | 35 | 65 |
| 2[a] | 1 | **Cat-4** | - | 37 | 63 |
| 3[b] | 1 | **Cat-2** | - | 36 | 64 |
| 4[b] | 1 | **Cat-4** | - | 35 | 65 |
| 5[c] | 1 | **Cat-1** | 54 | 1 | 45 |
| 6[c] | 1 | **Cat-2** | - | **25** | **74** |
| 7[c] | 1 | **Cat-3** | - | 32 | 68 |
| 8[c] | 1 | **Cat-4** | | 32 | 68 |
| 9[c] | 2 | **Cat-1** | 34 | 1 | 65 |
| 10[c] | 2 | **Cat-2** | - | **1** | **99** |
| 11[c] | 2 | **Cat-3** | - | 23 | 77 |
| 12[c] | 2 | **Cat-4** | - | 2 | 98 |

Reaction conditions: 1 mol% cat.; $H_2$ = 50 bar; at 80°C; 18 hours; [a] Trifluoroethanol (TFE) as solvent; [b] Time = 48 hours in TFE, [c] *n*-heptane as solvent; [d] Product distribution (%) determined by GC-FID analysis using internal standard (tetradecane). All reactions were performed in duplicate.

No significant difference in the product ratio was noticed after 48 hours (Table 3, entries 3 and 4). The selectivity towards cyclohexanol (**1c**) improved to 74% (Table 3, entry 6) upon changing the solvent to n-heptane and was almost similar in other cases. Excellent selectivity (>98%, for **2c**) was observed in the hydrogenation of propiophenone under the same reaction condition using **Cat-2** and **Cat-4** (Table 3, entries 10 and 12). On the other hand, **Cat-1** was found to be less selective in the production of saturated alcohol (**1-2c**) compared to the other complexes in the hydrogenation of both substrates. No hydrodeoxygenated alkane (**1-2d**) was detected in any of these reactions. It should be stated that the active catalyst is believed to be heterogeneous rhodium nanoparticles, stabilized by the NHCs and able to coordinate molecular hydrogen and ketones in order to perform the hydrogenation (as in the case of Zheng[29] and Glorius[25]). Although these theories are so far only speculative, ongoing studies are focusing on establishing the true nature of the catalyst and its exact composition.

## Conclusion

A new, versatile and efficient synthetic route to [Rh(acac)(CO)(NHC)] complexes was developed. *In situ* FT-IR monitoring provided insights into the reaction mechanism. The complexes were employed to establish a linear correlation between their IR carbonyl stretching band frequencies and the TEP of the NHCs. Catalytic tests were performed and showed great potential for aromatic hydrogenation and reduction of C-heteroatoms double bonds using these well-defined complexes as pre-catalysts. These early reactivity studies are quite promising, and ongoing studies will aim to understand their catalytic performance as well as how their easy synthesis can further assist the community in understanding ligand electronic effects.

## Experimental Section

### General information

#### Synthesis and characterization of rhodium complexes

All reactions were performed in scintillation vials under air. Solvents and reagents were used as received without any further purification. Elemental analyses were performed at Namur University, 61 rue de Bruxelles, 5000, Namur, Belgium. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-300, 400 or 500 MHz spectrometers at room temperature using $CDCl_3$ or $CD_2Cl_2$ as solvent. Chemical shifts (ppm) are referenced to the residual solvent peak. Coupling constants (J) are given in Hertz. All FT-IR measurement were performed with a Mettler Toledo ReactIR 15 and measured in a 0.05 M solution in dichloromethane.

#### Catalytic reactions

Acetophenone and Propiophenone were obtained from Merck and directly used in catalysis. *n*-Heptane was dried over Na/benzophenone and distilled. Trifluoroethanol (TFE) was purchased from Fluorochem and degassed prior to use. NMR spectra were recorded on Avance 400 ($^1$H: 400, $^{13}$C: 100 MHz) instruments operating at the denoted spectrometer frequency given in Megahertz (MHz) for the specified nucleus using $CDCl_3$ as solvent. Product distribution in the hydrogenation experiments, GC conversion and GC-MS were determined by GC-FID, Agilent HP6890 instrument with FID detector, column HP530 m x 250 mm x 0.25 µm. GC Method details:- $T_0$ = 30°C, ramp = 8°C/ min, $T_1$ = 280°C, $t_{hold}$ = 10 min, $T_1$ = 280°C, ramp = 8°C/ min, $T_2$ = 320°C, $t_{hold}$ = 10 min, $T_2$ = 280°C, ramp = 8°C/ min, $T_3$ = 320°C, $t_{hold}$ = 5 min ($T_0$ is the injection temperature, then the column is heated to $T_1$ (ramp), $t_{hold}$ is the holding time after heating to a certain temperature, similarly $T_2$ and $T_3$ are the temperature heated consecutively with specified ramp rate ). All catalytic reactions were carried out in 300 mL autoclaves (PARR Instrument Company).

#### Procedures and characterization

**General procedure for synthesis of [Rh(acac)(CO)(NHC)] complexes**

In a 20 mL vial were mixed 100 mg of [Rh(acac)$(CO)_2$] (0.39 mmol, 1 equiv.) and NHC·$HBF_4$ (0.39 mmol, 1 eq) in 4 mL of ethyl acetate and stirred at 40 °C under FT-IR monitoring until the solution is stabilized at the desired temperature. Then 5 equivalents of the selected base were added to the solution, and the mixture was stirred at 40 °C until IR spectra showed complete disappearance of the rhodium precursor. The solvent was then slowly removed under vacuum to reach the solubility limit of the product, which was precipitated by addition of 10 mL of pentane. The product was collected by filtration, dried and analysed.

**[Rh(acac)(CO)(IMes)] (Cat-1)**

**Yield**: 96 %. **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.02 (s, 2 H, C**H**=C**H**), 6.96 (s, 4 H; $C^{Ar}$**H**), 5.19 (s, 1 H; $C^{acac}$**H**), 2.34 (s, 6 H; $C_{para}$-C**$H_3$**), 2.20 (s, 12 H; $C_{ortho}$-C**$H_3$**), 1.84 (s, 6 H; $C^{acac}H_3$), 1.70 (s, 6 H; $C^{acac}H_3$). **$^{13}$C NMR** (75 MHz, $CDCl_3$) $\delta$ (ppm) 190.9 (N-**C**-N), 189.8 (Rh-**C**O), 186.8 ($\mathbf{C}^{acac}$O), 184.3 ($\mathbf{C}^{acac}$O), 138.4 ($\mathbf{C}_{para}$), 136.3 ($\mathbf{C}^{Ar}$-N), 135.6 ($\mathbf{C}_{ortho}$), 129.0 ($\mathbf{C}_{meta}$H), 122.8 (**C**H=**C**H), 100.1 ($\mathbf{C}^{acac}$H), 27.6 ($\mathbf{C}^{acac}H_3$), 26.2 ($\mathbf{C}^{acac}H_3$), 21.1 ($\mathbf{C}^{acac}H_3$), 18.3 ($C_{ortho}$-**C**$H_3$). **IR** in DCM: v(CO) = 1956.9 $cm^{-1}$. **Elemental analysis** calcd (%): C 60.68, H 5.85, N 5.24. Found: C 60.39, H 5.88, N 5,13.

**[Rh(acac)(CO)(IPr)] (Cat-2)**

**Yield**: 85 %. **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.46 (t, $J$ = 7.7 Hz, 2 H, $C_{para}$**H**), 7.29 (d, $J$ = 7.7 Hz, 4H; $C_{meta}$**H**), 7.09 (s, 2 H, C**H**=C**H**), 5.22 (s, 1 H; $C^{acac}$**H**), 2.92 (hept, $J$ = 6.8 Hz, 4 H; C**H**(-$CH_3$)$_2$), 1.83 (s, 6 H; $C^{acac}H_3$), 1.79 (s, 6 H; $C^{acac}H_3$), 1.27 (d, $J$ = 6.8 Hz, 12 H, CH-C**$H_3$**), 1.12 (d, $J$ = 6.8 Hz, 12 H, $C^{IPr}H_3$). **$^{13}$C NMR** (75 MHz, $CDCl_3$) $\delta$ (ppm) 146.2 ($\mathbf{C}_{para}$), 136.4 ($\mathbf{C}^{Ar}$-N), 129.7 (**C**H=**C**H), 124.5 ($\mathbf{C}_{ortho}$), 123.9 ($\mathbf{C}_{meta}$H), 99.8 ($\mathbf{C}^{acac}$H), 28.4 (**C**H(-$CH_3$)$_2$), 27.9 ($\mathbf{C}^{acac}H_3$), 27.6 ($\mathbf{C}^{acac}H_3$), 26.1 (CH-**C**$H_3$), 22.7 (CH-**C**$H_3$). **IR** in DCM: v(CO) = 1962.3 $cm^{-1}$. **Elemental analysis** calcd (%): C 64.07, H 7.01, N 4.53. Found: C 63.67, H 6.94, N 4.42.

**[Rh(acac)(CO)(IPr*)] (Cat-3)**

**Yield**: 99 %. **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 7.14 (s, 20 H, $C^{Ar}$**H**), 7.10-7.02 (m, 12 H, m, $C^{Ar}$**H**), 6.81-6.73 (m, 12 H, s, $C^{Ar}$**H**), 6.00 (s, 4 H, s, C**H**-$Ph_2$), 5.20 (s, 2 H, C**H**=C**H**), 5.20 (s, 1 H, $C^{acac}$**H)**, 2.20 (s, 6 H, s, $C^{Ar}$-C**$H_3$**), 2.06 (s, 3 H, s, $C^{acac}H_3$), 0.66 (s, 3 H, s, $C^{acac}H_3$). **$^{13}$C NMR** (75 MHz, $CDCl_3$) $\delta$ (ppm) 186.4 (d, $J_{C\text{-}Rh}$= 47 Hz, N-**C**-N), 143.9 (C), 143.6 (C), 141.7 (C), 138.1 (C), 136.5 (C), 130.4 (CH), 130.4, 129.5 (CH), 128.1 (CH), 127.8 (CH), 126.2 (CH), 126.0 (CH), 123.8 (CH), 100.7 ($\mathbf{C}^{acac}$H) 51.1 (**C**H(-$Ph_2$), 27.6 ($\mathbf{C}^{acac}H_3$), 26.5 ($\mathbf{C}^{acac}H_3$), 21.7 ($\mathbf{C}_{para}H_3$). **IR** in DCM: v(CO) = 1965.8 $cm^{-1}$. Data are in agreement with reported values.[20]

**[Rh(acac)(CO)(SIMes)] (Cat-4)**

**Yield**: 97 %. **$^1$H NMR** (300 MHz, $CDCl_3$) $\delta$ (ppm) 6.91 (s, 4 H; $C^{Ar}$**H**), 5.16 (s, 1 H; $C^{acac}$**H**), 3.91 (s, 4 H, C**$H_2$**-C**$H_2$**), 2.39 (s, 12 H; $C_{ortho}$-C**$H_3$**), 2.28 (s, 6 H; $C_{para}$-C**$H_3$**), 1.80 (s, 6 H; $C^{acac}H_3$), 1.74 (s, 6 H; $C^{acac}H_3$). **$^{13}$C NMR** (75 MHz, $CDCl_3$) $\delta$ (ppm) 207.2 (d, $J_{C\text{-}Rh}$ = 53.6 Hz, N-**C**-N) 190.2 (d, $J$ = 82.0 Hz, Rh-**C**O), 186.7 ($\mathbf{C}^{acac}$O), 184.2 ($\mathbf{C}^{acac}$O), 137.5 ($\mathbf{C}_{para}$), 136.7 ($\mathbf{C}^{Ar}$-N), 136.4 ($\mathbf{C}_{ortho}$), 129.3 ($\mathbf{C}_{meta}$H), 100.1 ($\mathbf{C}^{acac}$H), 50.9 (**C**$H_2$-**C**$H_2$), 27.6 ($\mathbf{C}^{acac}H_3$), 26.4 ($\mathbf{C}^{acac}H_3$), 21.1 ($C_{para}$-**C**$H_3$), 18.5 ($C_{ortho}$-**C**$H_3$). **IR** in DCM: v(CO) = 1960.5 $cm^{-1}$. Data are in agreement with reported values.[20]

**[Rh(acac)(CO)(SIPr)] (Cat-5)**

**Yield**: 99% %. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.36 (t, $J$ = 7.7 Hz, 2 H, $C_{para}$**H**), 7.24 (d, $J$ = 7.7 Hz, 4H; $C_{meta}$**H**), 3.99 (s, 4 H, C**$H_2$**-C**$H_2$**), 5.18 (s, 1 H; $C^{acac}$**H**), 3.40 (hept, $J$ = 6.8 Hz, 4 H; C**H**(-$CH_3$)$_2$), 1.80 (s, 6 H; $C^{acac}H_3$), 1.79 (s, 6 H; $C^{acac}H_3$), 1.34 (d, $J$ = 6.7 Hz, 12 H, CH-C**$H_3$**), 1.27 (d, $J$ = 6.8 Hz, 12 H, $C^{IPr}H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ (ppm) 210.9 (d, $J_{Rh\text{-}C}$ = 53 Hz, **C**-Rh), 190.6 (d, $J_{Rh\text{-}C}$ = 82 Hz, Rh-**C**O), 186.6 (s, $\mathbf{C}^{acac}$-O), 184.7 (s, $\mathbf{C}_{acac}$-O), 147.3 ($\mathbf{C}_{para}$), 137.1 ($\mathbf{C}^{Ar}$-N), 129.0 ($\mathbf{C}_{ortho}$), 124.6 ($\mathbf{C}_{meta}$H), 100.0 ($\mathbf{C}^{acac}$H), 54.1 (**C**$H_2$-**C**$H_2$), 28.7 (**C**H(-$CH_3$)$_2$), 28.0 ($\mathbf{C}^{acac}H_3$), 27.7 ($\mathbf{C}^{acac}H_3$), 26.6 (CH-**C**$H_3$), 23.9 (CH-**C**$H_3$). **IR** in DCM: v(CO) = 1965.3 $cm^{-1}$. Data are in agreement with reported values.[20]

**General procedure for catalysis**

All the hydrogenation experiments were performed in a stainless-steel autoclave charged with an insert suitable for up to 8 reaction vessels (4 mL vials) with teflon mini stirring bars. In a typical experiment, a reaction vessel is charged with 1 mol% of defined Rh-NHC complex and stirred for 10-15 mins in the appropriate solvent (1 mL). Then the desired substrates (0.2 mmol) were added to the reaction vessel and the vessels were placed in a high-pressure autoclave. First the autoclave was purged once with nitrogen and two times with hydrogen. Finally, it was pressurized at 50 bars of $H_2$ pressure at 80 ° C for the defined time. After the desired reaction time, the autoclave was depressurized, and the products were analysed by GC-FID using tetradecane as internal standard.

## Acknowledgements

We gratefully acknowledge VLAIO (SBO project CO2PERATE), the Moonshot project D2M for support. The Special Research Fund (BOF) of Ghent University is also acknowledged for starting and project grants to SPN. Umicore AG is thankfully acknowledged for generous gifts of materials.

*Dedicated to the memory of Professor Victor Snieckus*.

**Keywords:** Carbene ligands • Hydrogenation • Rhodium • Tolman Electronic structure

[1] (a) Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.*, **2020**, *120*, 1981-2048; (b) K. Ota, K. Nagao, H. Ohmiya, *Org. Lett.*, **2020**, *22*, 3922-3925; (c) A. Cervantes-Reyes, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Adv. Synth. Catal.*, **2020**, *362*, 12, 2523-2533; (d) A. Cook, S. Prakash, Y.-L. Zheng, S. G. Newman, *J. Am. Chem. Soc.*, **2020**, *142*, 8109-8115; (e) K. Iwai, M. Ono, Y. Nanjo, T. Ema, *ACS Omega*, **2020**, *5*, 10207-10216; (f) T. Biberger, R. J. Zachmann, A. Fürstner, *Angew. Chem. Int. Ed.*, **2020**, *59*, 42, 18423-18429; (g) W. Smit, M. Foscato, G. Occhipinti, V. R. Jensen, *ACS Catal.*, **2020**, *10*, 6788-6797.

[2] (a) D. Sivanesan, B. Seo, C.-S. Lim, D. Choi, T. Kim, H.-G. Kim, *Polym. Chem.*, **2020**, *11*, 2511-2518; (b) F. Quintin, J. Pinaud, F. Lamaty, X. Bantreil, *Organometallics*, **2020**, *39*, 636-639; (c) W. J. Wolf, T.-P. Lin, R. H. Grubbs, *J. Am. Chem. Soc.*, **2019**, *141*, 17796-17808; (d) M. McGraw, E. Y.-X. Chen, *ACS Catal.*, **2018**, *8*, 9877-9887.

[3] (a) J.-Gong Yang, K. Li, J. Wang, S. Sun, W. Chi, C. Wang, X. Chang, C. Zou, W.-P. To, M.-D. Li, X. Liu, W. Lu, H.-X. Zhang, C.-M. Che, Y. Chen, *Angew. Chem. Int. Ed.*, **2020**, *59*, 6915-6922; (b) M. Blanco, P. Álvarez, C. Blanco, M. V. Jiménez, J. Fernández-Tornos, J. J. Pérez-Torrente, L. A. Oro, R. Menéndez, *ACS Catal.*, **2013**, *3*, 1307-1317; (c) J. Li, L. Wang, Z. Zhao, X. Li, X. Yu, P. Huo, Q. Jin, Z. Liu, Z. Bian, C. Huang, *Angew. Chem. Int. Ed.*, **2020**, *59*, 8210-8217.

[4] (a) N. Marion, S.P. Nolan, *Chem. Soc. Rev.*, **2008**, *37*, 1776-1782 (b) G.C. Fortman, S.P. Nolan, *Chem. Soc. Rev.*, **2011**, *40*, 5151-5169 (c) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 8, 3708-3742

[5] H. Clavier, S.P. Nolan, ***Chem. Commun.***, **2010**, *46*, 841-861.

[6] (a) C.A. Tolman, *J. Am. Chem. Soc.*, **1970**, *92*, 2953-2956 (b) C.A. Tolman, *Chemical Reviews*, **1976***, 77***(3)**,* 313–348.

[7] D.G. Gusev, *Organometallics* **2009**, *28*, 22, 6458-6461

[8] (a) R. Dorta, E.D. Stevens, C.D. Hoff, S.P. Nolan, *J. Am. Chem. Soc.*, **2003**, *125*, 35, 10490-10491. (b) R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, *J. Am. Chem. Soc.*, **2005**, *127*, 8, 2485-2495. (c) H.V. Huynh, *Chem. Rev.*, **2018**, *118*, 19, 9457-9492

[9] S. Wolf, H. Plenio, *J. Organomet. Chem.*, **2009**, *694*, 1487-1492

[10] C.A. Urbina-Blanco, X. Bantreil, H. Clavier, A.M.Z. Slawin, S.P. Nolan, *J. Org. Chem.*, **2010**, *6*, 1120-1126.

[11] R.A. Kelly, H. Clavier, S. Giudice, N.M. Scott, E.D. Stevens, J. Bordner, I. Samardjiev, C.D. Hoff, L. Cavallo, S.P. Nolan, *Organometallics*, **2008**, *27*, 202-210.

[12] S. Leuthäußer, D. Schwarz, H. Plenio, *Chem. Eur. J.*, **2007**, *13*, 7195-7203.

[13] A.B.P. Lever, *Inorg. Chem.*, **1990**, *29*, 1271-1285

[14] (a) H.V. Huynh, Y. Han, R. Jothibasu, J.A. Yang, *Organometallics*, **2009**, *28*, 5395-5404. (b) Q. Teng, H.V.A. Huynh, *Dalton Trans.*, **2017**, *46*, 614-627. (c) S. Guo, H. Sivaram, D. Yuan, H.V. Huynh, *Organometallics*, **2013**, *32*, 3685-3696.

[15] O. Back, M. Henry-Ellinger, C.D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.*, **2013**, *52*, 2939-2943.

[16] (a) D.J. Nelson, A. Collado, S. Manzini, S. Meiries, A.M.Z. Slawin, D.B. Cordes, S.P. Nolan, *Organometallics*, **2014**, *33*, 2048-2058. (b) S.V.C. Vummaleti, D.J. Nelson, A. Poater, A. Gómez-Suárez, D.B. Cordes, A.M.Z. Slawin, S.P. Nolan, L. Cavallo, *Chem. Sci.*, **2015**, *6*, 1895-1904.

[17] K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.*, **2015**, *2015*, 2416-2425.

[18] (a) O. Kühl, *Coord. Chem. Rev.*, **2005**, *249*, 693-704. (b) L. Chen, P. Ren, B.P. Carrow, *J. Am. Chem. Soc.*, **2016**, *138*, 20, 6392-6395.

[19] S. Serron, J. Huang, S.P. Nolan, *Organometallics*, **1998**, *17*, 4, 534-539.

[20] (a) M.S. Datt, J.J. Nair, S. Otto, *J. Org. Chem.*, **2005**, *690*, 14, 3422-3426. (b) G. Berthon-Gelloz, M.A. Siegler, A.L. Spek, B. Tinant, J.N.H. Reekc, I.E. Markó, *Dalton Trans.*, **2010**, *39*, 1444-1446.

[21] (a) A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun.*, **2013**, *49*, 5541-5543. (b) O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.*, **2013**, *49*, 10483-10485. (c) C. M. Zinser, F. Nahra, M. Brill, R. E. Meadows, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.*, **2017**, *53*, 7990-7993. (d) C. M. Zinser, K. G. Warren, R. E. Meadows, F. Nahra, A. M. Al-Majid, A. Barakat, M. S. Islam, S. P. Nolan, C. S. J. Cazin, *Green Chem.*, **2018**, *20*, 3246-3252. (e) C. M. Zinser, K. G. Warren, F. Nahra, A. Al-Majid, A. Barakat, M. S. Islam, S. P. Nolan, C. S. J. Cazin, *Organometallics*, **2019**, *38*, 2812-2817; (f) S. G. Guillet, V. A. Voloshkin, M. Saab, M. Beliš, K. V. Hecke, F. Nahra, S. P. Nolan, *Chem. Commun.*, **2020**, *56*, 5953-5956. (g) N. V. Tzouras, F. Nahra, L. Falivene, L. Cavallo, M. Saab, K. V. Hecke, A. Collado, C. J. Collett, A. D. Smith, C. S. J. Cazin, S. P. Nolan, *Chem. Eur. J.*, **2020**, *26*, 4515-4519. (h) B. Landers, O. Navarro, *Eur. J. Inorg. Chem.*, **2012**, 2980-2982. (i) S. Zhua, R. Liang, H. Jiang, *Tetrahedron* **2012**, *68*, 7949-7955. (j) R. Visbal, A. Laguna, M.C. Gimeno, *Chem. Commun.*, **2013**, *49*, 5642-5644. (k) T. Scattolin, S.P. Nolan, *Trends Chem.*, **2020**, *2*, 8, 721-736.

[22] Note that Plenio has adapted our procedure for Au and Cu to [Rh(COD)(NHC)Cl] systems: R. Savka, H Plenio, *Dalton Trans.*, **2015**, *44*, 891-893.

[23] J.G. de Vries, C.J. Elsevier, C. J. in *The Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, **2008**.

[24] S. Kaufhold. L. Petermann, R. Staehle, S. Rau, *Coord. Chem. Rev.*, **2015**, *304–305*, 73-87.

[25] (a) M.P. Wiesenfeldt, Z. Nairoukh, W. Li, F. Glorius, *Science*, **2017**, *357*, 908-912. (b) Z. Nairoukh, M. Wollenburg, C. Schlepphorst, K. Bergander, F. Glorius, *Nat. Chem.*, **2019**, *11*, 264-270.

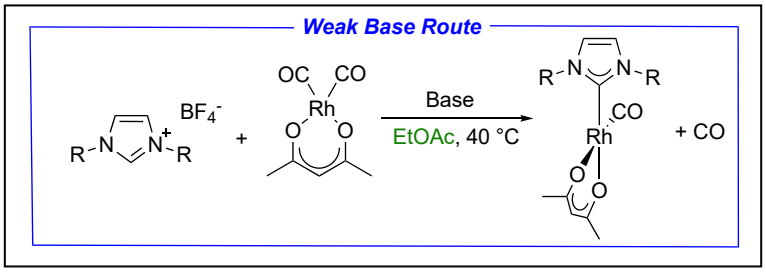
[26] (a) M. Wollenburg, D. Moock, F. Glorius, *Angew. Chem. Int. Ed.*, **2019**, *58*, 6549-6553. (b) M.P. Wiesenfeldt, T. Knecht, C. Schlepphorst, F. Glorius, *Angew. Chem. Int. Ed.*, **2018**, *57*, 8297-8300.

[27] Under catalytic hydrogenation conditions related pre-catalysts are transformed into Rh nanoparticles, see: (a) B. L. Tran, J. L. Fulton, J. C. Linehan, J. A. Lercher, R. M. Bullock, *ACS Catal.* **2018**, *8*, 8441-8449; (b) B. L. Tran, J. L. Fulton, J. C. Linehan, M. Balasubramanian, J. A. Lercher, R. M. Bullock, *ACS Catal.* **2019**, *9*, 4106-4114. The presence of dark solid material after catalysis is suspected to be such NP and these are presently being studied.

[28] G. Moos, M. Emondts, A. Bordet, W. Leitner, *Angew. Chem. Int. Ed.*, **2020**, *59*, 11977-11983

[29] Y. Wei, B. Rao, X. Cong, X. Zeng, *J. Am. Chem. Soc.*, **2015**, *137*, 9250-9253.

## Entry for the Table of Contents




**Simpler is better:** An operationally simple synthetic protocol for the synthesis of [Rh(acac)(CO)(NHC)] complexes is described. Insights into the mechanism are provided using operando spectroscopy. The spectroscopic fingerprints of these complexes are correlated to NHCs reported electron-donating descriptor values. An assessment of these complexes in catalytic applications is reported, showing promising results in the catalytic hydrogenation of aromatic ketones.