

# Oxidative addition of MeI to cationic Rh(I) carbonyl complexes with pyridyl bis(carbene) ligands

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## Abstract

A series of cationic Rh(I) carbonyl complexes of the form  $[\text{Rh}(\text{CO})(\text{L})]\text{PF}_6$  (where L = 2,6-bis(alkylimidazol-2-ylidene)-pyridine; alkyl = Me (**1a**), Et (**1b**),  $\text{CH}_2\text{Ph}$  (**1c**)) have been prepared by the reactions of  $[\text{Rh}(\text{CO})_2(\text{OAc})]_2$  with diimidazolium pyridine salts in the presence of  $\text{NEt}_3$ . The  $\nu(\text{CO})$  values for **1** are ca.  $1982\text{ cm}^{-1}$ , indicating that the N-heterocyclic carbene ligands impart high electron density on the Rh(I) centres, despite the overall cationic charge. Each of the Rh(I) complexes reacts with MeI to form two isomeric Rh(III) methyl species, and a third unidentified species. Kinetic measurements on the MeI oxidative addition reactions give second-order rate constants (MeCN,  $25^\circ\text{C}$ ) of  $0.0927$ ,  $0.0633$  and  $0.0277\text{ M}^{-1}\text{ s}^{-1}$  for **1a**, **1b** and **1c**, respectively. Comparison of these data with those for related Rh(I) carbonyl complexes shows that **1** have remarkably high nucleophilicity for cationic species.

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**Keywords:** Rhodium; Carbonyl; Carbene; Oxidative addition; Methyl iodide

## 1. Introduction

Since the isolation of a stable N-heterocyclic carbene (NHC) by Arduengo et al. [1], there has been substantial interest in the use of these species as ligands in transition metal chemistry. The donor power of NHC ligands is considered to be greater than that of trialkylphosphines, prompting a range of investigations seeking to exploit their properties in homogeneous catalysis [2–5]. Currently, the chemistry of complexes containing tridentate pincer NHC ligands that incorporate pyridine subunits is being explored. Most of the tridentate pincer bis(carbene) ligands reported so far are Pd-based and have been used in catalytic C–C bond formation reactions (e.g. Suzuki, Heck and Sonogashira) [5–8].

The oxidative addition of iodomethane to square planar  $d^8$  metal centres is a fundamental process in organometallic chemistry, with significant implications for catalysis, especially when followed by methyl migration to give an acetyl derivative as in the catalytic carbonylation of methanol [9]. It is of interest how the steric and electronic properties of the ancillary ligands can affect the rates of the oxidative addition and migratory insertion steps. Recent examples in the literature have investigated the effects of monodentate [10,11], bidentate [12–14] and tridentate ligands [15,16] on the reactivity of neutral rhodium(I) carbonyl complexes.

In this paper, we report the synthesis and characterisation of cationic Rh(I) carbonyl complexes of tridentate pyridyl bis(carbene) ligands and the oxidative addition reactions of these complexes with iodomethane. It is found that despite the cationic charge, the high electron density bestowed on the Rh(I) centre by the NHC donor ligands results in nucleophilicity higher than some related neutral complexes.

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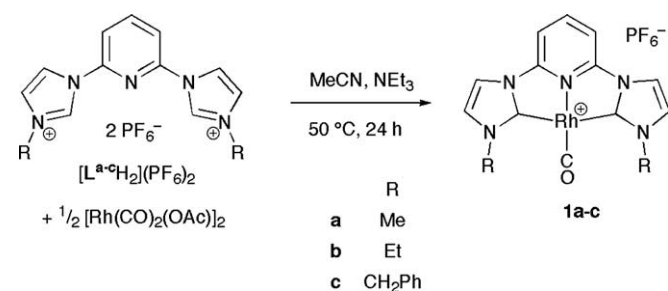
## 2. Results and discussion

### 2.1. Synthesis and characterisation of Rh(I) complexes

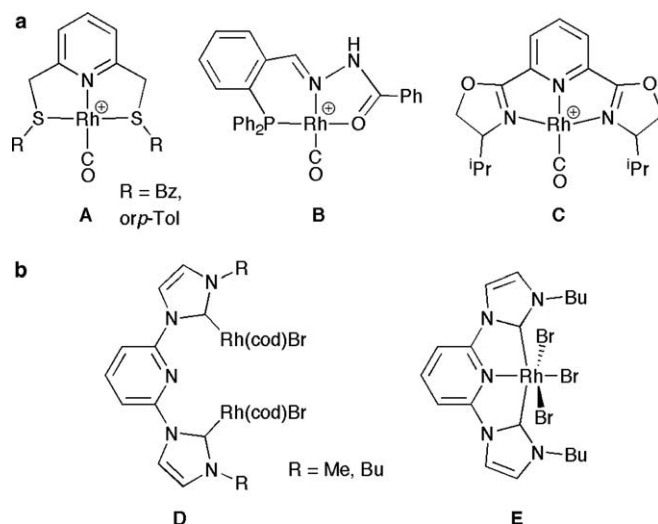
The 2,6-bis(alkylimidazolium)pyridine salts,  $[L^{a-c}H_2](PF_6)_2$ , were prepared by methods previously reported in the literature [17,18]. The molecular structure of the benzyl derivative,  $L^cH_2(PF_6)_2$ , was determined by X-ray crystallography and details are given in the [Supplementary Material](#). Complexation to rhodium was achieved by formation of the of the pyridyl bis(carbene) ligands in situ from the bis(imidazolium) pyridine salts, as illustrated in [Scheme 1](#). The Rh(I) dimer  $[Rh(CO)_2(OAc)]_2$  was chosen as the rhodium precursor, since its acetate ligands can participate in deprotonation of the bis(imidazolium) pyridine salt. However, to achieve the necessary double deprotonation,  $NEt_3$  was also added as an external base. The products,  $[Rh(CO)(L^{a-c})]PF_6$  (**1a–c**) were isolated and fully characterised by spectroscopy and elemental analysis.

The  $^1H$  NMR spectra of complexes **1a–c** are consistent with symmetrical tridentate coordination of the pincer carbene. Thus, signals are observed due to pairs of equivalent protons in the 4- and 5-positions on the two carbene units and in the 3- and 5-positions on the pyridyl ring, as well as signals due to equivalent *N*-alkyl groups. The IR spectra (in MeCN) show  $\nu(CO)$  absorptions at 1982, 1983 and 1982  $cm^{-1}$ , respectively, for **1a–c**. These relatively low  $\nu(CO)$  frequencies indicate very high electron density on the rhodium centre considering the cationic charge. The frequency shift with respect to other cationic rhodium(I) carbonyl complexes (e.g.  $\nu(CO)$  2015, 2018 and 2001  $cm^{-1}$ , respectively, for **A** [15,19], **B** [20] and **C** [21] in [Scheme 2\(a\)](#)) provides further evidence of the strong donor ability of the NHC-based ligands.

It is noteworthy that previous attempts to synthesise Rh(I) complexes containing pincer ligands of this type have resulted in formation of dinuclear products in which the pyridyl bis(carbene) ligand acts as a bidentate bridging ligand (complex **D**, [Scheme 2\(b\)](#)) [22,23]. However, a Rh(III) complex, **E**, with the pincer coordination mode is known [22].



Scheme 1. Synthesis and numbering scheme for ligands **L** and complexes **1**.



Scheme 2. (a) Examples of cationic Rh(I) carbonyl complexes containing tridentate ligands. (b) Coordination of pyridyl bis(carbene) complexes to Rh(I) and Rh(III).

### 2.2. Reactions of Rh(I) complexes with iodomethane

Treatment of **1a** with MeI in MeCN at 25  $^\circ C$  resulted in the decay of its  $\nu(CO)$  band at 1982  $cm^{-1}$ , accompanied by the formation of three new absorptions at 2007, 2044 and 2073  $cm^{-1}$  ([Fig. 1](#)). Analogous IR spectroscopic observations were made for the reactions of the other Rh(I) complexes with MeI (giving  $\nu(CO)$  bands at 2005, 2042, 2070  $cm^{-1}$  and 2007, 2042, 2072  $cm^{-1}$  for the reactions of **1b** and **1c**, respectively). The two higher frequency product bands in each case are consistent with Rh(III) methyl products resulting from oxidative addition, whereas the third product band is rather low in frequency for such an assignment. No IR bands were observed in the acetyl  $\nu(CO)$  region near 1700  $cm^{-1}$ , indicating the absence of migratory

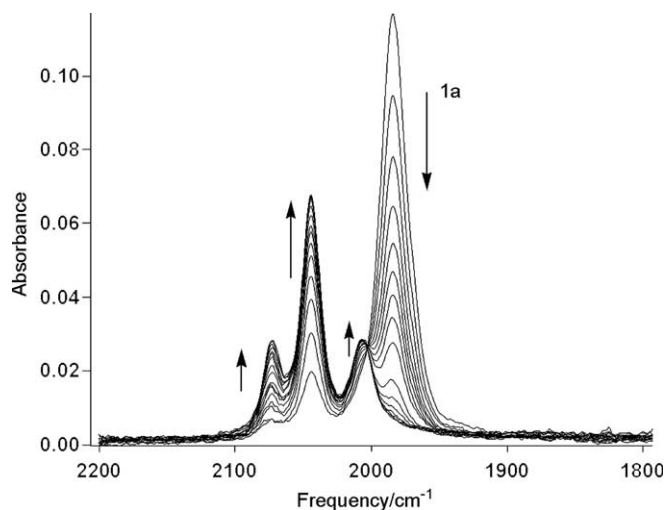
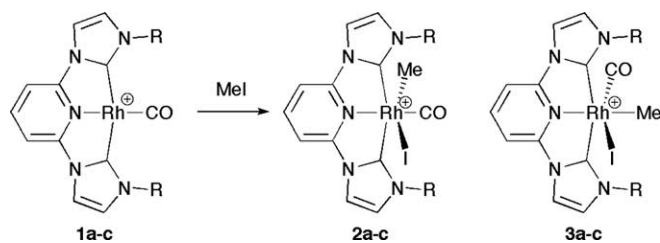


Fig. 1. Series of IR spectra for the reaction of **1a** with MeI (0.064 M in MeCN). The arrows indicate the evolution of each band during the reaction.

insertion under the conditions of these experiments. Initially, for the reaction of **1a**, the product  $\nu(\text{CO})$  band at  $2044\text{ cm}^{-1}$  was the most intense, but slow conversion to the species with  $\nu(\text{CO})$  at  $2073\text{ cm}^{-1}$  occurred on standing. The solid product obtained on removal of solvents had elemental analysis consistent with formulation as  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{Me})(\text{I})]\text{PF}_6$ . The  $^1\text{H}$  NMR spectrum of the product displayed doublets at  $\delta$  0.51 and  $\delta$  0.004 (both with  $^2J_{\text{Rh-H}}$  2.1 Hz) having an intensity ratio 11:1 indicating the presence of two isomers of  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{Me})(\text{I})]^+$ . Signals for the tridentate ligand show only small shifts from those in the precursor, **1a**, and indicate that a plane of symmetry (through Rh, the pyridyl N and perpendicular to the tridentate ligand plane) is maintained. The IR band at  $2073\text{ cm}^{-1}$  is assigned to the major isomer, with  $\delta^1\text{H}$  0.51. It was not found to be possible to isolate a single product isomer. The species responsible for the third weak product  $\nu(\text{CO})$  band at  $2007\text{ cm}^{-1}$  has not so far been identified.

The reaction of **1a** with MeI was also monitored using  $^{13}\text{C}$  NMR spectroscopy. A sample of  $^{13}\text{CO}$  enriched **1a** was dissolved in  $\text{CD}_3\text{CN}$  in an NMR tube. The initial spectrum showed a single intense doublet in the rhodium carbonyl region ( $\delta$  193.55 ppm,  $^1J_{\text{Rh-C}}$  62.0 Hz). To the NMR tube was then added  $^{13}\text{CH}_3\text{I}$  (1.3–3 equiv/Rh) and spectra were recorded at intervals over a period of a week. Doublets due to two new rhodium carbonyl species were generated over time at  $\delta$  189.53 ( $^1J_{\text{Rh-C}}$  61.0 Hz) and 197.22 ppm ( $^1J_{\text{Rh-C}}$  61.5 Hz) along with doublets for two rhodium methyl species at  $\delta$   $-1.08$  ( $^1J_{\text{Rh-C}}$  20.0 Hz) and  $-3.50$  ppm ( $^1J_{\text{Rh-C}}$  18.1 Hz). No  $^2J_{\text{C-C}}$  coupling was observed for any of these signals, indicating that the carbonyl and methyl ligands are not mutually *trans*. The spectroscopic evidence therefore suggests formation of two isomers **2a** and **3a** of formula  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{Me})(\text{I})]\text{PF}_6$ , each having methyl *cis* to carbonyl, as shown in Scheme 3. No evidence was found for the third possible isomer, having iodide *trans* to the pyridyl N; the third product  $\nu(\text{CO})$  band is rather too low in frequency to be consistent with such a species. The data do not confirm whether **2a** or **3a** is the major isomer. Unfortunately, no crystals suitable for a crystallographic structure determination have so far been obtained.

Some preliminary tests on the reactivity of the oxidative addition products have been performed on a spectroscopic scale. Addition of  $\text{AgBF}_4$  to an orange acetonitrile solution



Scheme 3. Reactivity of complexes **1** with MeI.

of  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{Me})(\text{I})]\text{PF}_6$  resulted in precipitation of  $\text{AgI}$  and formation of a yellow species with  $\nu(\text{CO})$   $2095\text{ cm}^{-1}$ . The shift to high frequency is consistent with abstraction of iodide to give a di-cationic complex,  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{NCMe})(\text{Me})]^{2+}$ , probably containing coordinated solvent. Subsequent addition of  $\text{Bu}_4\text{NI}$  regenerated an orange solution which displayed only the  $\nu(\text{CO})$  band at  $2073\text{ cm}^{-1}$ , indicating reformation of the major isomer of  $[\text{Rh}(\text{CO})(\text{L}^{\text{a}})(\text{Me})(\text{I})]^+$ . Similarly, iodide abstraction from  $[\text{Rh}(\text{CO})(\text{L}^{\text{b}})(\text{Me})(\text{I})]\text{PF}_6$  resulted in a single  $\nu(\text{CO})$  band at  $2095\text{ cm}^{-1}$  and subsequent addition of iodide reformed a single isomer of  $[\text{Rh}(\text{CO})(\text{L}^{\text{b}})(\text{Me})(\text{I})]^+$  with  $\nu(\text{CO})$   $2070\text{ cm}^{-1}$  and a  $^1\text{H}$  doublet for Rh–Me at  $\delta$  0.65. Although the iodide abstraction-addition sequence appears to result in the formation of a single isomer, the spectroscopic data do not allow definitive assignment of the geometrical arrangement of ligands.

### 2.3. Kinetics of oxidative addition

FTIR spectroscopy was employed to monitor the reactions of **1a–c** with MeI in MeCN as a function of temperature and  $[\text{MeI}]$ . Pseudo-first-order conditions were maintained by keeping the  $[\text{MeI}]$  in large excess compared with  $[\text{Rh}]$ . Fig. 1 shows a typical series of spectra and an example of the absorbance versus time plots is shown in Fig. 2. The data for the decay of the starting complexes (**1a–c**) are well fitted by exponential curves, from which pseudo-first-order rate constants ( $k_{\text{obs}}$ ) can be obtained. Plots of  $k_{\text{obs}}$  vs.  $[\text{MeI}]$  are linear, indicating the reactions to be first order in MeI and hence second order overall. Second-order rate constants ( $k_2$ ) are given in Table 1. Variable-temperature kinetic data over the range  $15\text{--}35\text{ }^\circ\text{C}$

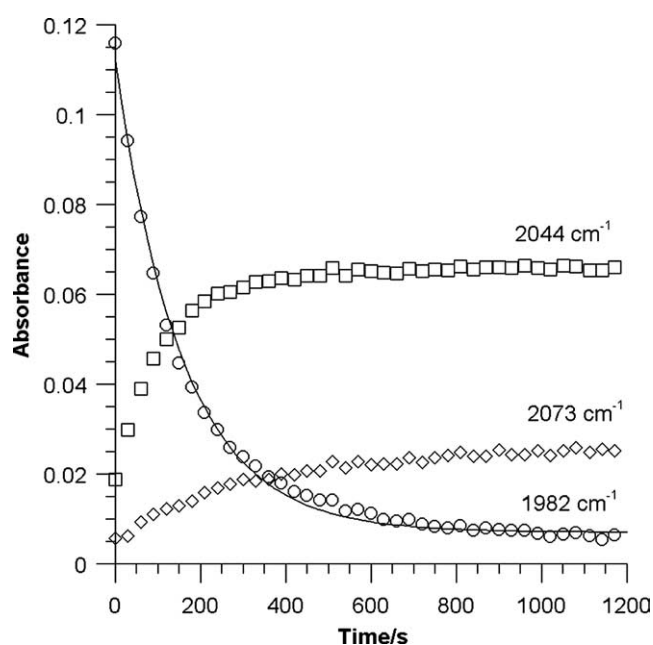


Fig. 2. Kinetic plot showing the growth and decay of  $\nu(\text{CO})$  bands during reaction of **1a** with MeI (0.064 M in MeCN,  $25\text{ }^\circ\text{C}$ ).

Table 1  
Kinetic data for oxidative addition reactions of MeI with **1a–c**

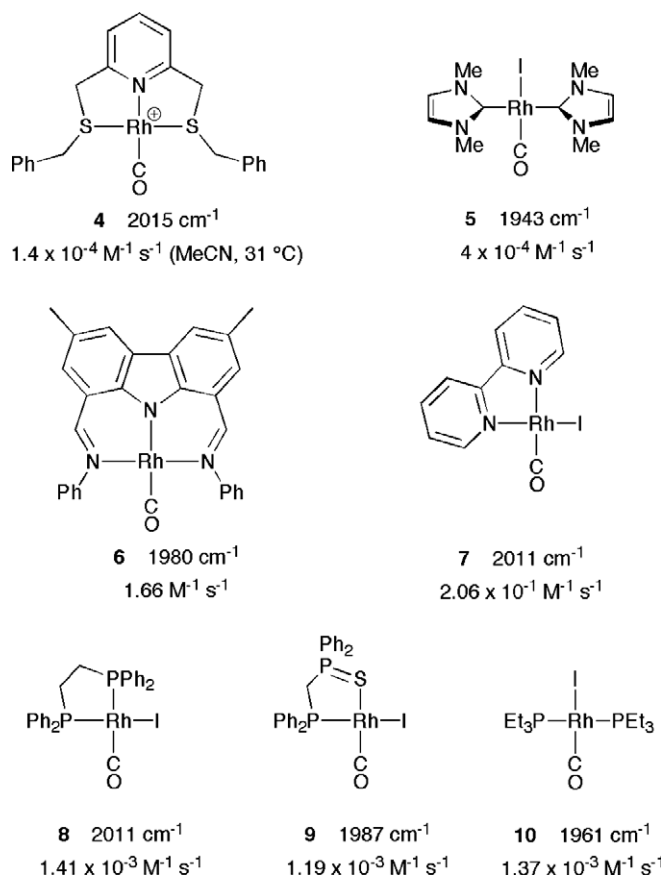
Complex	$\nu(\text{CO})/\text{cm}^{-1}$	$10^2 k_2/\text{M}^{-1} \text{s}^{-1}$ (25 °C)	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$
<b>1a</b>	1982	9.27	20 ( $\pm 2$ )	-198 ( $\pm 6$ )
<b>1b</b>	1983	6.33	24 ( $\pm 3$ )	-188 ( $\pm 6$ )
<b>1c</b>	1982	2.77	34 ( $\pm 3$ )	-162 ( $\pm 8$ )

were also measured, and satisfactory Eyring plots of these data gave the apparent activation parameters listed in Table 1. It should be noted that these rate constants and activation parameters correspond to the rate of decay of the reactant Rh(I) complexes and will contain contributions from the processes leading to each of the observed products if these form by independent routes. It is possible, however, that the oxidative addition products arise from a common reactive intermediate formed in an initial step from the reactant and MeI. In this case, the measured kinetic data would be valid for the first step. The clean second-order kinetics for disappearance of **1a–c** are consistent with a bimolecular reaction with MeI, but do not provide information about subsequent product isomerisation steps. The apparent activation entropies are all large and negative, as frequently found for oxidative addition of MeI to square planar  $d^8$  metal complexes, which is generally thought to proceed via an  $S_N2$  mechanism [10,11,13–16].

The kinetic data for oxidative addition of MeI to **1a–c** indicate a decrease in the reactivity on increasing the size of the carbene *N*-alkyl group. This is consistent with some steric inhibition of nucleophilic attack by the Rh(I) centre on MeI, since changing the alkyl group has little electronic effect, as judged by the  $\nu(\text{CO})$  frequencies.

The oxidative addition rate constants can be compared with those obtained for some related complexes shown in Scheme 4. Kinetic measurements have recently been reported for the reaction of MeI with a cationic Rh(I) carbonyl complex (**4**) containing a tridentate S, N, S donor ligand, 2,6-bis(benzylthiomethyl)pyridine [15,24]. Addition of MeI to **4** results in two unstable Rh(III) methyl isomers which undergo migratory insertion to give an acetyl complex. The second-order rate constant for MeI oxidative addition to **4** is 2–3 orders of magnitude lower than those for the pyridyl bis(carbene) complexes **1a–c**. This can be ascribed to the weaker donation by thioethers relative to NHC ligands, as supported by the significantly higher  $\nu(\text{CO})$  frequency of **4**. The cationic Rh(I) carbonyl complexes **B** and **C** shown in Scheme 2(a) also undergo oxidative addition of MeI but kinetic data have not been reported.

Interestingly complexes **1a–c** are significantly more reactive than the neutral iodicarbonyl complex **5**, which contains two monodentate NHC ligands coordinated *trans* to each other [11]. The  $\nu(\text{CO})$  value of **5** is considerably lower than those of the cations **1a–c**, consistent with a more electron-rich Rh centre. However, the nucleophilicity of **5** is moderated by steric effects of the *N*-methyl substituents. The monodentate NHC ligands lie approximately perpen-



Scheme 4. Some Rh(I) carbonyl complexes with their  $\nu(\text{CO})$  values and MeI oxidative addition rate constants (25 °C in  $\text{CH}_2\text{Cl}_2$  except where stated).

dicular to the Rh coordination plane, thereby placing the *N*-methyl substituents in positions where they inhibit approach to both of the vacant axial coordination sites. In **1a–c** tethering of the NHC units to the pyridyl moiety causes the *N*-alkyl groups to be directed away from the axial coordination sites, as illustrated by the X-ray crystal structure reported for an octahedral Rh(III) tribromide complex (Scheme 2) [22]. Thus, steric inhibition is not pronounced, facilitating nucleophilic attack by the Rh centres of **1a–c**. It is also noteworthy that the more crowded steric environment in **5** results in rapid methyl migration subsequent to oxidative addition of MeI, whereas stable Rh(III) methyl complexes are formed from **1a–c**.

We recently reported that the bis(imino)carbazole complex, **6** has very high reactivity towards MeI [16]. Its rate constant for oxidative addition is ca. 18 times larger than the that for **1a**. This can largely be ascribed to the change in charge between cationic **1a–c** and neutral **7**, since both systems are relatively free of steric hindrance. However, the  $\nu(\text{CO})$  values of **1a–c** are only 2–3  $\text{cm}^{-1}$  higher than that of **6**. A number of neutral complexes of the type  $[\text{Rh}(\text{CO})(\text{L}-\text{L})\text{I}]$ , containing bidentate ligands, have also been the subject of recent investigations. The most reactive of these is the bipyridyl complex **7** [14], which has a rate constant for MeI addition ca. double that of **1a**. The P, P

and P, S chelate complexes, **8** and **9** [13] (along with the monodentate bis(PEt<sub>3</sub>) complex, **10** [10]) are somewhat less reactive, with rate constants 65–80 times smaller than for **1a**.

These comparisons reveal that complexes **1a–c** exhibit remarkably high nucleophilicity, considering their cationic charge. Indeed, they have higher reactivity than many neutral Rh(I) carbonyl complexes (and are even ca. 3000 times more reactive than the anionic carbonylation catalyst, [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>−</sup>). It appears that complexes of ligands with relatively hard C and N donor atoms have higher intrinsic nucleophilicity than those with phosphines.

### 3. Conclusion

A series of cationic rhodium complexes containing tridentate pyridyl bis(carbene) ligands have been prepared and characterised. Their relatively low carbonyl stretching frequencies demonstrate the strong donor power of pincer carbene ligands. Reaction of the each of the rhodium(I) complexes with MeI leads to the formation of a pair of isomeric rhodium(III) methyl species and a third unknown species. Kinetic studies show that the oxidative addition reactions are first order in both the Rh(I) complex and MeI, with second-order rate constants significantly larger than that reported for a related cationic bis(thioether)pyridyl Rh(I) carbonyl complex. Indeed, the nucleophilicity of cations **1a–c** is comparable with (and greater than some) neutral Rh(I) complexes. The *N*-alkyl substituents of the pincer carbene ligand do not have a large effect on reactivity and do not create sufficient steric crowding to strongly inhibit oxidative addition or to promote migratory CO insertion.

## 4. Experimental section

### 4.1. Materials

All solvents used for synthesis or kinetic experiments were distilled and degassed prior to use the following literature procedures [25]. Synthetic procedures were carried out utilizing standard Schlenk techniques. Nitrogen and carbon monoxide were dried through a short (20 × 3 cm diameter) column of molecular sieves (4 Å), which was regularly regenerated. Carbon monoxide was also passed through a short column of activated charcoal to remove the iron pentacarbonyl impurity. The rhodium precursor [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> [26], 2,6-bis(methylimidazolium) pyridine diiodide [17], 2,6-bis(ethylimidazolium) pyridine diiodide [17] and 2,6-bis(benzylimidazolium) pyridine dibromide [18] were synthesised according to the literature procedures. Methyl iodide (Aldrich) was distilled over calcium hydride and stored in foil-wrapped Schlenk tubes under nitrogen and over mercury to prevent formation of I<sub>2</sub>. NaOAc, NEt<sub>3</sub>, KPF<sub>6</sub> (Aldrich), and RhCl<sub>3</sub> · xH<sub>2</sub>O (PMO) were used as supplied.

### 4.2. Instrumentation

FTIR spectra were measured using a Matson Genesis Series spectrometer, controlled by WIN-FIRST software running on a Viglen 486 PC. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker AC250 spectrometer fitted with a Bruker B-ACS60 automatic sample changer operating in pulse Fourier transform mode, using the solvent as reference. Elemental analyses were performed using a Perkin–Elmer Model 2400 elemental analyser.

### 4.3. Synthesis of ligand precursors

#### 4.3.1. L<sup>a</sup>H<sub>2</sub> · 2PF<sub>6</sub>

An aqueous solution of 2,6-bis(methylimidazolium)pyridine diiodide (2.12 g, 4.3 mmol) was added dropwise to an aqueous solution of KPF<sub>6</sub> (1.59 g, 8.65 mmol). The resulting white precipitate was filtered and dried under vacuum; yield 1.67 g (73%). Anal. Calc. for C<sub>13</sub>H<sub>15</sub>F<sub>12</sub>N<sub>5</sub>P<sub>2</sub>: C, 29.39; H, 2.85; N, 13.18. Found: C, 29.29; H, 2.70; N, 13.10%. <sup>1</sup>H NMR (CD<sub>3</sub>CN; δ) 4.00 (s, 6H, Me), 7.61 (bs, 2H, H4-Im), 7.90 (d, 2H, H3-Py), 8.18 (bs, 2H, H5-Im), 8.42 (t, 1H, H4-Py), 9.42 (bs, 2H, H2-Im).

#### 4.3.2. L<sup>b</sup>H<sub>2</sub> · 2PF<sub>6</sub>

An analogous procedure to that described above for L<sup>a</sup>H<sub>2</sub> · 2PF<sub>6</sub> was employed, using 2,6-bis(ethylimidazolium) pyridine diiodide (2.67 g, 4.96 mmol) and KPF<sub>6</sub> (1.89 g, 10.27 mmol); yield 1.50 g (54%). Anal. Calc. for C<sub>15</sub>H<sub>19</sub>F<sub>12</sub>N<sub>5</sub>P<sub>2</sub>: C, 32.21; H, 3.42; N, 12.52. Found: C, 32.03; H, 3.29; N, 12.64%. <sup>1</sup>H NMR (CD<sub>3</sub>CN; δ) 1.58 (t, 6H, CH<sub>2</sub>Me), 4.35 (q, 4H, CH<sub>2</sub>Me), 7.68 (bs, 2H, H4-Im), 7.91 (d, 2H, H3-Py), 8.22 (s, 2H, H5-Im), 8.43 (t, 1H, H4-Py), 9.43 (bs, 2H, H2-Im).

#### 4.3.3. L<sup>c</sup>H<sub>2</sub> · 2PF<sub>6</sub>

An analogous procedure to that described above for L<sup>a</sup>H<sub>2</sub> · 2PF<sub>6</sub> was employed, using 2,6-bis(benzylimidazolium) pyridine dibromide (0.79 g, 1.43 mmol) and KPF<sub>6</sub> (0.55 g, 3.56 mmol); yield 0.60 g (61%). Anal. Calc. for C<sub>25</sub>H<sub>23</sub>F<sub>12</sub>N<sub>5</sub>P<sub>2</sub>: C, 43.94; H, 3.39; N, 10.25. Found: C, 43.60; H, 3.20; N, 9.98%. <sup>1</sup>H NMR (CD<sub>3</sub>CN; δ) 5.48 (s, 4H, CH<sub>2</sub>Ph), 7.40–7.54 (m, 10H, Ph), 7.62 (bs, 2H, H4-Im), 7.90 (d, 2H, H3-Py), 8.21 (bs, 2H, H5-Im), 8.41 (t, 1H, H4-Py), 9.53 (bs, 2H, H2-Im). Crystals of L<sup>c</sup>H<sub>2</sub> · 2PF<sub>6</sub> suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a chloroform solution. The crystallographic data are provided as [Supplementary Material](#) and have been deposited (CCDC 273301).

### 4.4. Synthesis and reactions of Rh complexes

#### 4.4.1. [Rh(CO)<sub>2</sub>(OAc)]<sub>2</sub>

Pentane (80 cm<sup>3</sup>), presaturated with CO, was added to a mixture of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> (0.965 g, 2.48 mmol) and NaOAc (1.72 g, 21.02 mmol) under a CO atmosphere

at room temperature [27]. The mixture was stirred for 24 h and then filtered to remove sodium salts. The solvent was removed in vacuo, and the solid residue purified by vacuum sublimation, to give a red-green dichroic crystalline solid; yield 0.815 g (88%). IR ( $\text{CH}_2\text{Cl}_2$   $\nu(\text{CO})/\text{cm}^{-1}$ ): 2073, 2022.

#### 4.4.2. $[\text{Rh}(\text{CO})(\text{L}^a)]\text{PF}_6$ (**1a**)

$[\text{Rh}(\text{CO})_2(\text{OAc})_2]$  (0.012 g, 0.03 mmol), 1,1'-(pyridine-2,6-di-yl)bis(3-methyl-1H-imidazolium)dihexafluorophosphate (0.035 g, 0.07 mmol) and triethylamine (50  $\mu\text{l}$ , 0.35 mmol) were placed in a 50  $\text{cm}^3$  Schlenk flask under  $\text{N}_2$ . Acetonitrile (5  $\text{cm}^3$ ) was added, and the mixture was stirred overnight at 50 °C. The solvent was then removed in vacuo, and the resulting purple residue was dissolved in the minimum amount of THF. Precipitation of the product as a purple solid was achieved by addition of hexane. The liquid phase was removed by cannula and the solid was dried in vacuo overnight; yield 0.023 g (69%). Anal. Calc. for  $\text{C}_{14}\text{H}_{13}\text{F}_6\text{N}_5\text{OPRh}$ : C, 32.64; H, 2.54; N, 13.59. Found: C, 32.19; H, 2.38; N, 13.24%. IR ( $\text{CH}_3\text{CN}$   $\nu(\text{CO})/\text{cm}^{-1}$ ): 1982.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ;  $\delta$ ): 3.95 (s, 6H, Me), 7.20 (d, 2H, H4-Im), 7.70 (d, 2H, H3-Py), 7.94 (d, 2H, H5-Im), 8.32 (t, 1H, H4-Py).

#### 4.4.3. $[\text{Rh}(\text{CO})(\text{L}^b)]\text{PF}_6$ (**1b**)

An analogous procedure to that described above for **1a** was employed, using  $[\text{Rh}(\text{CO})_2(\text{OAc})_2]$  (0.068 g, 0.18 mmol), 1,1'-(pyridine-2,6-di-yl)bis(3-ethyl-1H-imidazolium) dihexafluorophosphate (0.208 g, 0.37 mmol) and triethylamine (250  $\mu\text{l}$ , 1.74 mmol); yield 0.081 g (41%). Anal. Calc. for  $\text{C}_{16}\text{H}_{17}\text{F}_6\text{N}_5\text{OPRh}$ : C, 35.38; H, 3.15; N, 12.89. Found: C, 35.23; H, 3.00; N, 12.76%. IR ( $\text{CH}_3\text{CN}$   $\nu(\text{CO})/\text{cm}^{-1}$ ): 1983.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ;  $\delta$ ): 1.39 (t, 6H,  $\text{CH}_2\text{Me}$ ), 3.95 (q, 4H,  $\text{CH}_2\text{Me}$ ), 7.21 (d, 2H, H4-Im), 7.24 (d, 2H, H3-Py), 7.58 (d, 2H, H5-Im), 8.02 (t, 1H, H4-Py).

#### 4.4.4. $[\text{Rh}(\text{CO})(\text{L}^c)]\text{PF}_6$ (**1c**)

An analogous procedure to that described above for **1a** was employed, using  $[\text{Rh}(\text{CO})_2(\text{OAc})_2]$  (0.061 g, 0.16 mmol), 1,1'-(pyridine-2,6-di-yl)bis(3-benzyl-1H-imidazolium) dihexafluorophosphate (0.218 g, 0.319 mmol) and triethylamine (250  $\mu\text{l}$ , 1.744 mmol); yield 0.19 g (85%). Anal. Calc. for  $\text{C}_{26}\text{H}_{21}\text{F}_6\text{N}_5\text{OPRh}$ : C, 46.79; H, 3.17; N, 10.49. Found: C, 46.58; H, 3.06; N, 10.02%. IR ( $\text{CH}_3\text{CN}$   $\nu(\text{CO})/\text{cm}^{-1}$ ): 1982.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ;  $\delta$ ): 5.23 (s, 4H,  $\text{CH}_2\text{Ph}$ ), 7.23–7.34 (m, 10H, Ph), 7.35 (d, 2H, H4-Im), 7.38 (d, 2H, H3-Py), 7.71 (d, 2H, H5-Im), 8.12 (t, 1H, H4-Py).

#### 4.4.5. $[\text{Rh}(\text{CO})(\text{L}^a)]\text{PF}_6$

A gentle stream of  $^{13}\text{CO}$  was bubbled through a solution of **1a** (0.086 g, 0.169 mmol) in acetonitrile (5  $\text{cm}^3$ ) for 30 min. The solvent was removed in vacuo and dried overnight; yield 0.079 g (92%). IR ( $\text{CH}_3\text{CN}$   $\nu(^{13}\text{CO})/\text{cm}^{-1}$ ): 1938.

#### 4.4.6. $[\text{Rh}(\text{CO})(\text{L}^a)(\text{Me})(\text{I})]\text{PF}_6$

Iodomethane (3  $\text{cm}^3$ , 48.2 mmol) was added to a solution of **1a** (0.017 g, 0.034 mmol) in acetonitrile (5  $\text{cm}^3$ ) and stirred overnight. The solvent was then removed and the sample dried in vacuo overnight; yield 0.017 g (74%). Anal. Calc. for  $\text{C}_{15}\text{H}_{16}\text{F}_6\text{IN}_5\text{OPRh}$ : C, 27.42; H, 2.45; N, 10.66. Found: C, 27.22; H, 2.28; N, 10.59%. IR ( $\text{CH}_3\text{CN}$   $\nu(\text{CO})/\text{cm}^{-1}$ ): 2044 (minor), 2073 (major), 2007 (w).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ;  $\delta$ ): 0.51, 0.004 (both d, ratio 11:1, total 3H,  $^2J_{\text{Rh-H}}$  2.1 Hz, RhMe isomers), 3.92 (s, 6H, Me), 7.32 (d, 2H, H4-Im), 7.72 (d, 2H, H3-Py), 7.96 (d, 2H, H5-Im), 8.34 (t, 1H, H4-Py).

#### 4.4.7. Iodide abstraction experiments

A sample of  $[\text{Rh}(\text{CO})(\text{L}^b)(\text{Me})(\text{I})]\text{PF}_6$  was freshly prepared by dissolving **1b** (30 mg, 0.054 mmol) in MeCN (3  $\text{cm}^3$ ) MeCN, to which MeI (1  $\text{cm}^3$ ) was added. After stirring for 10 min (the purple solution having turned orange) the solvent was removed in vacuo. Addition of  $\text{AgBF}_4$  (10.6 mg, 0.0543 mmol) to an MeCN solution of this sample of  $[\text{Rh}(\text{CO})(\text{L}^b)(\text{Me})(\text{I})]\text{PF}_6$  resulted in a precipitate of AgI and the orange solution became green and then yellow. After filtration through Celite, the IR spectrum of the yellow solution displayed a  $\nu(\text{CO})$  band at 2096  $\text{cm}^{-1}$ . On addition of excess  $\text{Bu}_4\text{NI}$  (157.6 mg, 0.43 mmol) the solution became orange, with  $\nu(\text{CO})$  2070  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) showed a single Rh–Me doublet at  $\delta$  0.66 ( $^2J_{\text{Rh-H}}$  2.1 Hz). An analogous procedure starting with **1a** resulted in a yellow solution with  $\nu(\text{CO})$  2096  $\text{cm}^{-1}$  after treatment with  $\text{AgBF}_4$  and reformation of the orange Rh–Me species with  $\nu(\text{CO})$  2073  $\text{cm}^{-1}$  and  $\delta^1\text{H}$  0.51 on addition of  $\text{Bu}_4\text{NI}$ .

#### 4.5. Kinetic experiments

Samples for the kinetic runs were prepared by placing the required amount of freshly distilled iodomethane in a 5  $\text{cm}^3$  graduated flask, which was then made up to the mark with acetonitrile. A portion of this solution was used to record a background spectrum. Another portion (typically 500  $\mu\text{l}$ ) was added to the solid complex (typically 5–8  $\mu\text{mol}$ ) in a sample vial to give a reaction solution containing 10–15 mM [Rh]. A portion of the reaction solution was quickly transferred to the IR cell and the kinetic experiment was started. Pseudo-first-order conditions were employed, with a least a 10-fold excess of MeI, relative to the metal complex. The IR cell (0.5 mm path length,  $\text{CaF}_2$  windows) was maintained at constant temperature throughout the kinetic run by a thermostated jacket. Spectra were scanned in the metal carbonyl  $\nu(\text{CO})$  region (2200–1600  $\text{cm}^{-1}$ ) and saved at regular time intervals under computer control. After the kinetic run, absorbance versus time data for the appropriate  $\nu(\text{CO})$  frequencies were extracted and analysed off-line using Kaleidagraph curve-fitting software. The decays of the bands **1** were all well fitted by exponential curves with correlation coefficients  $\geq 0.999$ ,

to give pseudo-first-order rate constants. Each kinetic run was repeated at least twice to check reproducibility, the  $k_{\text{obs}}$  values being averaged values with component measurements deviating from each other by  $\leq 5\%$ .

#### 4.6. *In situ* NMR experiments

Samples were prepared by placing 90 mg of  $^{13}\text{C}$ O labelled **1a** in a 5 mm diameter NMR tube. The tube was purged with nitrogen and 0.75 cm<sup>3</sup> of dry CD<sub>3</sub>CN (also under nitrogen) was added to dissolve the complex. To the complex solution was added  $^{13}\text{CH}_3\text{I}$  (1.3–3 equiv/Rh) by syringe and the sample was shaken. The  $^{13}\text{C}$  NMR spectrum of the reaction mixture was monitored periodically using a Bruker AC250 spectrometer.

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#### Appendix A. Supplementary data

Tables of kinetic data and X-ray crystallographic data. CCDC 273301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.08.010](https://doi.org/10.1016/j.jorganchem.2005.08.010).

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