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# Vibrational solvatochromism of rhodium pybox carbonyl complexes mediated by hydrogen bonding

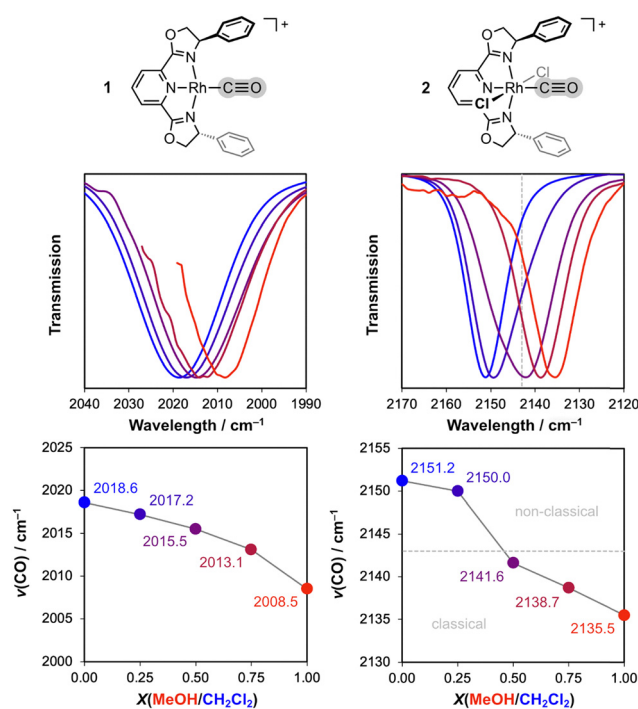
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**The carbonyl stretching frequencies of structurally related classical and non-classical rhodium carbonyl complexes are significantly red-shifted by methanol enrichment in solution and rationalised in terms of the nature of the hydrogen bonding interactions involved using *ab initio* molecular dynamics simulations.**

The  $\nu(\text{CO})$  vibrational frequencies of metal-carbonyl complexes are key spectroscopic handles in organometallic chemistry, facilitating reaction monitoring and providing insight into the metal-mediated activation of CO.<sup>1</sup> Terminal CO coordination is classically characterised by red-shifted values of  $\nu(\text{CO})$  relative to free CO and interpreted using the Dewar-Chatt-Duncanson bonding model, wherein the CO bond is weakened by population of the  $\pi^*(\text{CO})$  orbitals through metal-to-ligand  $\pi$ -backbonding.<sup>2</sup> Contemporary theoretical analysis indicates that this charge transfer occurs alongside significant polarisation of the CO bond,<sup>3</sup> which renders  $\nu(\text{CO})$  sensitive to the local electrostatic environment and helps reconcile the existence of non-classical carbonyl complexes that exhibit shorter CO bond lengths and blue-shifted  $\nu(\text{CO})$  values relative to free CO (2143  $\text{cm}^{-1}$ ).<sup>4,5</sup> As the majority of organometallic chemistry is conducted in solution and the associated intermolecular interactions are primarily electrostatic in nature,<sup>6</sup> it is imperative that solvent effects are considered when interpreting differences in  $\nu(\text{CO})$ .<sup>7</sup> Building upon our recent work investigating the role of electrostatics in metal-carbonyl bonding,<sup>5,8</sup> we herein present a combined experimental and computational study examining how solvent influences the  $\nu(\text{CO})$  vibrational frequencies of the homologous rhodium(i) and rhodium(III) pybox carbonyl complexes **1** and **2** (Fig. 1). These complexes are an interesting test set as, when analysed by FT-IR spectroscopy in the routinely employed solvent dichloromethane, the

latter is characterised as a non-classical carbonyl complex with  $\nu(\text{CO}) = 2151 \text{ cm}^{-1}$ .<sup>9</sup>

Inspired by experimental and computational work on conceptually related organocarbonyl compounds, where values of  $\nu(\text{CO})$  are lowered in hydrogen bonding environments,<sup>10</sup> we have analysed **1** and **2** by FT-IR spectroscopy in binary mixtures of dichloromethane/methanol (Fig. 1). Red shifts are observed as concentration of the strongly H-bonding solvent methanol was increased, with  $\nu(\text{CO})$  ranging from 2018.6 to 2008.5  $\text{cm}^{-1}$  for **1** ( $\Delta\nu(\text{CO}) = -10.1 \text{ cm}^{-1}$ ) and 2151.2 to 2135.5  $\text{cm}^{-1}$  for **2** ( $\Delta\nu(\text{CO}) = -15.7 \text{ cm}^{-1}$ ). Similar differences are observed for

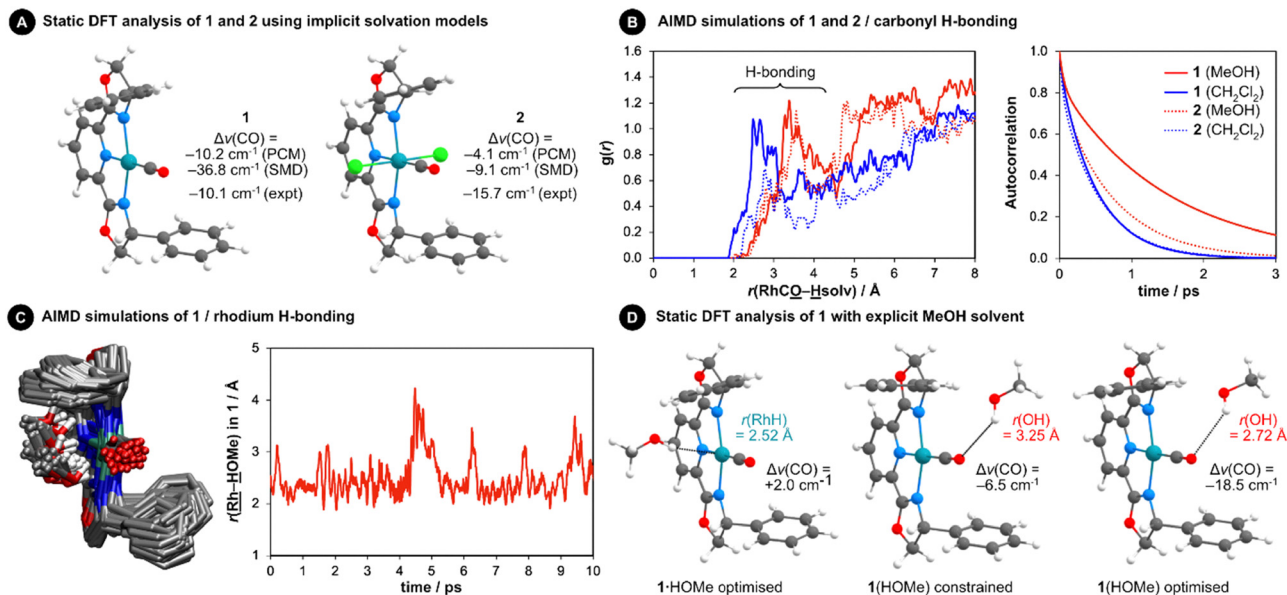


**Fig. 1** FT-IR analysis of rhodium(I) and rhodium(III) pybox carbonyl complexes **1** and **2** in binary mixtures of dichloromethane/methanol.  $[\text{BAR}_4\text{F}]^-$  counterions omitted for clarity.

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**Fig. 2** Computational analysis of rhodium(I) and rhodium(III) pybox carbonyl complexes **1** and **2** relevant to their observed vibrational solvatochromism in methanol vs. dichloromethane (cations only). Static DFT calculations were performed at the B3PW91/6-31G(d,p) (SDD for Rh) level of theory.<sup>13,14</sup> AIMD simulations were performed using the PBE functional and the DZVP-MOLOPT-GTH (DZVP-MOLOPT-SR-GTH for Rh) Gaussian plane-wave basis set, with the cut-off and relative cut-off set at 250 Ry and 80 Ry respectively, and dispersion effects captured through inclusion of Grimme's D3 dispersion correction.<sup>15</sup>  $\Delta\nu(\text{CO})$  for MeOH vs.  $\text{CH}_2\text{Cl}_2$  (A) and explicit MeOH vs. gas phase (D).

the dimethyl-pybox analogues of **1** ( $\Delta\nu(\text{CO}) = -12.3 \text{ cm}^{-1}$ ) and **2** ( $\Delta\nu(\text{CO}) = -13.9 \text{ cm}^{-1}$ ). The concave shape of the solvatochromic curve indicates that **1** is preferentially solvated by dichloromethane, while the point of inflection observed for **2** is attributed to dielectric enrichment and a reduced propensity for H-bonding.<sup>11</sup> The observed  $\Delta\nu(\text{CO})$  are substantial and can be put in context by reference to the  $11 \text{ cm}^{-1}$  difference in Tolman Electronic Parameter between the aryl and alkyl phosphines  $\text{PPh}_3$  and  $\text{PCy}_3$ .<sup>12</sup> Remarkably for **2** the red shift is large enough to merit a change in classification from a non-classical carbonyl complex in dichloromethane to a classical carbonyl complex in methanol.

Static DFT calculations using implicit solvation models failed to consistently reproduce the red shifts observed in pure methanol relative to dichloromethane (Fig. 2A).<sup>13</sup> Specifically,  $\Delta\nu(\text{CO})$  for **2** is underestimated by the polarizable continuum model (PCM), whereas that of **1** is overestimated by the solvation model based on density (SMD).<sup>14</sup> Both implicit models predict the rhodium(I) complex **1** to be more solvatochromic than the rhodium(III) complex **2**, contrary to experiment but consistent with how  $\nu(\text{CO})$  of these complexes are affected by an oriented external electric field (see SI, Fig. S18).

To more accurately capture solvation effects, we resorted to DFT-based *ab initio* molecular dynamics (AIMD) simulations, where dichloromethane or methanol molecules surrounding **1** and **2** are explicitly included in the calculations. The level of theory was selected based on previous work,<sup>5,15</sup> with simulations performed in the NVT ensemble at 298 K with a 0.5 fs time step, consistent with the timescale of an IR experiment. An equilibration phase of 5000 steps preceded a production run of 20 000 steps. Wannier-based analysis on the final 10 000 steps enabled ensemble calculation of  $\nu(\text{CO})$ , with the resulting

$\Delta\nu(\text{CO})$  values in excellent agreement with experiment ( $-9.8 \text{ cf. } -10.1 \text{ cm}^{-1}$  for **1**;  $-16.3 \text{ cf. } -15.7 \text{ cm}^{-1}$  for **2**).<sup>16</sup> Radial distribution functions traced between the carbonyl O atom and solvent protons revealed H-bonding interactions for **1** and **2**, with peaks between 2–3 Å for dichloromethane and 3–4 Å for methanol (Fig. 2B). The lifetime of these interactions, as quantified by an autocorrelation analysis,<sup>16</sup> show that methanol forms stronger, longer-lived H-bonds than dichloromethane, congruent with the red-shifted values of  $\nu(\text{CO})$  measured experimentally in methanol ( $\tau = 2.5 \text{ vs. } 0.9 \text{ ps}$  for **1**;  $\tau = 1.2 \text{ vs. } 0.9 \text{ ps}$  for **2**; Fig. 2B). All else being equal, the larger increase in H-bonding lifetime calculated for **1** ( $\tau_{\text{MeOH}}/\tau_{\text{CH}_2\text{Cl}_2} = 2.7$ ) than for **2** ( $\tau_{\text{MeOH}}/\tau_{\text{CH}_2\text{Cl}_2} = 1.3$ ) is, however, at odds with the magnitudes of  $\Delta\nu(\text{CO})$  measured experimentally, which imply the opposite trend.

From closer inspection of the AIMD trajectories, a persistent H-bond with the metal centre was uniquely identified for **1** in methanol (Fig. 2C). This solvent interaction is maintained throughout the entire simulation run, albeit for one reversible decoordination of  $<1 \text{ ps}$ , and characterised by an average  $\text{Rh} \cdots \text{H-O}$  distance of  $2.5(4) \text{ \AA}$ . To assess the impact on the value of  $\nu(\text{CO})$ , the geometry of this methanol adduct **1-HOMe** was extracted from the trajectory and analysed in the gas-phase using static DFT methods (Fig. 2D). The H-bond was retained upon optimisation and is characterised by a  $\text{Rh} \cdots \text{H}$  contact of  $2.52 \text{ \AA}$  and a  $\text{Rh} \cdots \text{H-O}$  angle of  $141^\circ$ . Subsequent Hessian analysis indicates that formation of **1-HOMe** induces a blue-shift in  $\nu(\text{CO})$  of  $+2.0 \text{ cm}^{-1}$  relative to **1**.<sup>17</sup> Following a similar static DFT analysis, red shifts in  $\nu(\text{CO})$  but of greater magnitude are calculated for carbonyl H-bonding using an explicit molecule of methanol, either constrained based on the AIMD data or



in a fully optimised geometry (Fig. 2D and Fig. S20). It therefore appears that the solvatochromic response for **1** in methanol reflects a balance between relatively short-lived H-bonding of the solvent with the carbonyl ligand, which induce large red-shifts in  $\nu(\text{CO})$  and more persistent H-bonding with the metal centre, which counteract lowering in  $\nu(\text{CO})$ .

This experimental/computational investigation reinforces the importance of electrostatics in metal-carbonyl bonding and, through examining changes in the  $\nu(\text{CO})$  vibrational frequency, demonstrates how activation of CO can be modulated by interaction with the solvent. The latter is exemplified by rhodium(III) complex **2**, for which vibrational solvatochromism in dichloromethane/methanol spans the non-classical/classical divide, and underscores why accurate comparison of  $\nu(\text{CO})$  values requires measurements to be made in the same solvent.<sup>7</sup> More broadly, our results show that solvent-induced spectral changes of metal carbonyl complexes can be understood in terms of dynamic H-bonding interactions and their lifetimes, as revealed by *ab initio* molecular dynamics simulations in combination with snapshot analysis by traditional, static DFT calculations.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI): synthesis and characterisation of the dimethyl pybox analogues of **1** and **2**, computational information and data, optimised geometries in XYZ format. See DOI: <https://doi.org/10.1039/d6cc02481e>.

CCDC under 2545198 (**1**) and 2545199 (**2**) contain the supplementary crystallographic data for this paper.<sup>18</sup>

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