

## Hidden heterogeneous catalysis

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Rhodium-catalysed hydrogenation of nitrous oxide

The hydrogenation of nitrous oxide is a thermodynamically favourable transformation relevant to the remediation of this potent greenhouse gas and ozone-depleting substance. Few homogeneous catalysts can operate under the aggressive reaction conditions involved, and our work highlights the potential for molecular complexes of platinum-group metals to decompose into catalytically active nanoparticles.

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We report on the discovery of “hidden” heterogeneous catalysis in the hydrogenation of nitrous oxide while assessing the catalytic activity of a rhodium(i) hydride complex supported by a nominally robust phosphine-based pincer ligand. Commercially available [Rh(COD)(OH)]<sub>2</sub> was subsequently identified as a more effective catalyst precursor, enabling the hydrogenation of nitrous oxide with an apparent turnover number >3000 at room temperature.

Nitrous oxide (N<sub>2</sub>O) is a long-lived gas that accumulates in the atmosphere, contributing to climate change as a potent greenhouse gas and leading to ozone depletion in the stratosphere.<sup>1</sup> Although chemical activation is challenging, exponentially increasing anthropogenic emissions of N<sub>2</sub>O make it imperative that energy efficient methods are developed to remediate point sources of this atmospheric pollutant.<sup>2</sup> Direct decomposition into N<sub>2</sub> and O<sub>2</sub> is encumbered by the formidable kinetic stability of N<sub>2</sub>O, necessitating temperatures >700 °C at atmospheric pressure.<sup>3</sup> While heterogeneous catalysts can promote this reaction (*ca.* 300–600 °C), variants where sacrificial reducing agents are added to facilitate removal of surface oxygen atoms are capable of operating at lower temperatures and more appealing from a remediation perspective.<sup>4</sup> In this context, the hydrogenation of N<sub>2</sub>O to afford N<sub>2</sub> and H<sub>2</sub>O is a thermodynamically favourable, yet undeveloped transformation, using either heterogeneous or homogeneous catalysts.

Of the limited examples of heterogeneous N<sub>2</sub>O hydrogenation described in the literature,<sup>5</sup> the use of platinum group metal catalysts is outstanding for the mild operating temperatures involved. For instance, ruthenium, rhodium,

## Rhodium-catalysed hydrogenation of nitrous oxide†

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palladium, and platinum supported on titania promote the hydrogenation of N<sub>2</sub>O between 50–150 °C, with activity increasing in the order Pd > Rh > Pt > Ru based on measurements made using a flow reactor.<sup>6</sup> Rhodium supported on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is also active under flow conditions and a TOF of 0.022 s<sup>-1</sup> was measured for the former at 72 °C.<sup>7</sup> Molecular complexes of the platinum group metals have additionally been investigated as homogeneous catalysts, with seminal work using ruthenium pincer complexes reported by Milstein in 2017 (Fig. 1).<sup>8</sup> A mechanism involving O-atom insertion into a Ru–H bond, coupled with bifunctional reactivity of the supporting PNP pincer ligand, was proposed and 417 TONs achieved over 48 h at 65 °C. More productive catalysts have since been identified,<sup>9,10</sup> including a remarkable rhodium-based system by Trincado and Grützmacher, during the preparation of this manuscript, which delivered 230 000 apparent TONs after 96 h at 65 °C (Fig. 1).<sup>11</sup>

Building upon our work with rhodium pincer complexes, which has included the isolation of well-defined Rh–N<sub>2</sub>O adducts,<sup>12</sup> we became interested in assessing the relative catalytic activity of the homologous series of complexes 1–3



Fig. 1 Late transition metal hydride complexes used as catalysts for the hydrogenation of nitrous oxide.

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**Table 1** Catalyst screening for the hydrogenation of N<sub>2</sub>O<sup>a</sup>

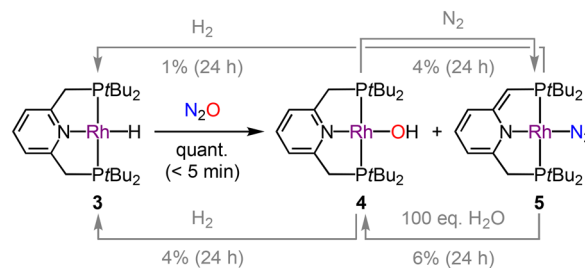
Entry	Catalyst (additive/variation)	[H <sub>2</sub> O]/M	TON
1	None	0.00	—
2	[Ru(PNP- <i>t</i> Bu)HCl(CO)] (+KO <i>t</i> Bu) <sup>b</sup>	0.03	5
3	[Ir(PNP- <i>t</i> Bu)H <sub>3</sub> ] 2	0.01	1
4	[Rh(PNP- <i>t</i> Bu)H] 3 <sup>c</sup>	0.90	174
5	[Rh(PNP- <i>t</i> Bu)H] 3 (+Hg)	0.01	2
6	[Rh(PNP- <i>t</i> Bu)H] 3 (THF → CyH)	<0.01	<1
7	[Rh(PNP- <i>t</i> Bu)(OH)] 4 <sup>c</sup>	0.75	146
8	[Rh(PNP- <i>t</i> Bu)N <sub>2</sub> ] 5 <sup>c</sup>	0.75	144
9	Rh/C <sup>d</sup>	0.24	47
10	[Rh(COD)(OH)] <sub>2</sub> 6 <sup>c</sup>	1.72	318
11	[Rh(COD)(OH)] <sub>2</sub> 6 ( <i>t</i> = 1 h) <sup>c</sup>	0.03	6

<sup>a</sup> Conditions: 10 μmol of catalyst/Rh in 2.0 mL of THF placed under ~1:2 H<sub>2</sub>/N<sub>2</sub>O (3 atm) within a 100 mL gas bulb with cold finger (126 mL water volume) and stirred at RT for 24 h. Conversion determined by <sup>1</sup>H NMR analysis using a mesitylene internal standard and averaged over duplicate runs. <sup>b</sup> No conversion observed in the absence of KO*t*Bu. <sup>c</sup> Generation of N<sub>2</sub> verified by head space analysis (GC-TCD). <sup>d</sup> Hydrogenation of the internal standard was observed. Similar activity is achieved in the absence of the internal standard.

(Fig. 1). Octahedral hydride complexes **1** (generated from [Ru(PNP-*t*Bu)(CO)HCl] and KO*t*Bu) and **2** have previously been assessed by Milstein and Suárez,<sup>8,9</sup> and we hypothesised that the component phosphine-based pincer ligand PNP-*t*Bu would be a thermally robust scaffold that would support the homogeneous hydrogenation of N<sub>2</sub>O using square-planar rhodium(i) hydride **3**.<sup>13,14</sup>

The hydrogenation of N<sub>2</sub>O was first examined at RT using 5 mM solutions of **1–3** in 2.0 mL THF, stirred within the cold finger of a 100 mL gas bulb pressurised with a ~1:2 mixture of H<sub>2</sub>/N<sub>2</sub>O (3 atm, Table 1). Under these net oxidising conditions, **1** and **2** showed very low catalytic activity, whereas **3** gave 174 apparent TONs over 24 h: as quantified by the formation of water by <sup>1</sup>H NMR spectroscopy with the generation of N<sub>2</sub> verified by GC-TCD analysis of the head space.

Encouraged by the high catalytic activity of **3**, we sought to understand the underlying mechanism. To this end, the reaction between **3** (20 mM) and N<sub>2</sub>O (2 atm) was examined *in situ* by NMR spectroscopy in *d*<sup>8</sup>-THF, revealing quantitative spectroscopic conversion of **3** into a ~1:1 mixture of the known rhodium(i) hydroxide complex **4** ( $\delta_{31P}$  55.6, <sup>1</sup>J<sub>RhP</sub> = 162 Hz) and dearomatized rhodium(i) dinitrogen complex **5** ( $\delta_{31P}$  66.6, <sup>1</sup>J<sub>RhP</sub> = 132 Hz; 63.1, <sup>1</sup>J<sub>RhP</sub> = 132 Hz; <sup>2</sup>J<sub>PP</sub> = 269 Hz) within 5 min at RT (Scheme 1).<sup>15</sup> This outcome is consistent with activation of N<sub>2</sub>O by O-atom insertion into the Rh–H bond,<sup>16</sup> followed by (partial) bifunctional elimination of water as proposed for **1** by Milstein.<sup>8</sup> Although independently isolated **4** and **5** are catalytically competent for the hydrogenation of N<sub>2</sub>O under the aforementioned conditions (Table 1), they react incompatibly slowly with H<sub>2</sub> at RT on a NMR reaction scale and, moreover, do not reform **3** cleanly (Scheme 1). Likewise, whilst **4** eliminated water to give **5** under an atmosphere of N<sub>2</sub> and treatment of **5** with excess water gave

**Scheme 1** Reactions of isolated **1–3** in *d*<sup>8</sup>-THF at RT.

**4**, both reactions are sluggish at RT and partial decomposition was observed during the former. This decomposition is attributed to the instability of **5** and a significant amount of PNP-*t*Bu oxide was produced when a 20 mM solution of **5** in *d*<sup>8</sup>-THF was placed under N<sub>2</sub>O (2 atm; 11% after 24 h at RT by <sup>31</sup>P NMR spectroscopy). No reaction with **4** was observed under the same conditions.

These observations, coupled with the deposition of dark residues on the reactor walls and observation of PNP-*t*Bu oxide by <sup>31</sup>P NMR spectroscopy when using **3** in catalysis, led us to question the homogeneous nature of the hydrogenation. The formation of 2.9 ± 0.4 nm rhodium nanoparticles was subsequently confirmed by TEM/EDX analysis of the post-catalysis reaction mixture (Fig. 2A), and their role in catalysis corroborated by a positive mercury drop test, in which addition of mercury almost completely inhibited catalysis using **3** (Table 1, entry 5).<sup>17</sup> The N<sub>2</sub>O hydrogenation observed for **3** is therefore not attributed to homogeneous catalysis as we hypothesized, but instead reconciled by the formation of catalytically-active rhodium nanoparticles from partial decomposition of **5** under the reaction conditions (generated from **3** + N<sub>2</sub>O or **4** – H<sub>2</sub>O, Scheme 1). Isolated **5** displays significantly enhanced stability in cyclohexane and, in further support of this conclusion, **3** is an ineffective catalyst for N<sub>2</sub>O hydrogenation when cyclohexane is used in place of THF as the reaction solvent (Table 1, entry 6).

Having concluded that **3** operates *via* heterogeneous catalysis, we sought to identify a more convenient source of rhodium to apply in the hydrogenation of N<sub>2</sub>O (Table 1). Commercially available Rh/C was first assessed under our conditions but gave only 47 apparent TONs over 24 h. The use of bench stable [Rh(COD)(OH)]<sub>2</sub> (**6**, COD = 1,5-cyclooctadiene) as a nanoparticle precursor was more promising,<sup>18</sup> with a catalytic turnover nearly double that of **3** recorded after 24 h. Disproportionately low turnover after 1 h is symptomatic of an induction period for **6** and post catalysis analysis of the different runs by SAXS suggests that activity may correlate with a greater degree of nanoparticle aggregation. For instance, particles of mean radius 26.6 nm were observed after 1 h, while after 24 h the scattering data are best modelled as a mixture containing particles with a mean radius of 58.6 nm (see ESI†). These changes in aggregation are also apparent from TEM/EDX analysis of the samples (Fig. 2B/C).



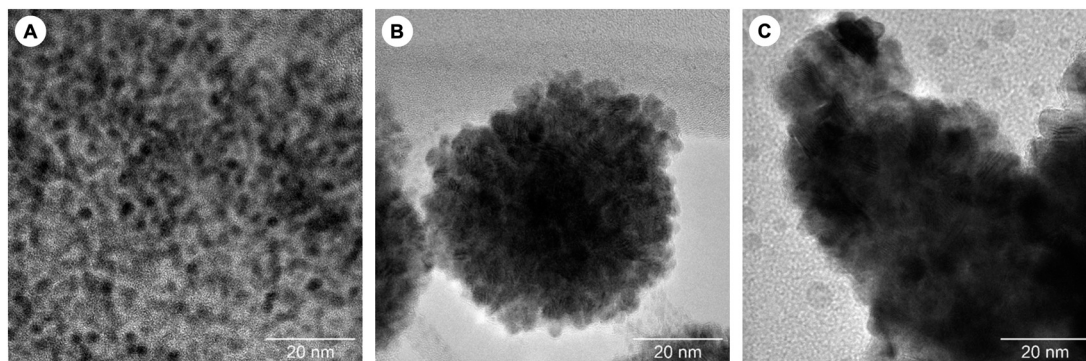


Fig. 2 TEM images taken from post catalysis reaction mixtures when using (A) **3**, (B) **6** (1 h run) and (C) **6** (24 h run).

To further explore the catalytic utility of **6**, the hydrogenation reaction was tested on a larger scale using a 250 mL gas bulb, under otherwise unoptimised reaction conditions: 5 mM  $[\text{Rh}(\text{COD})(\text{OH})_2]$  in 2.0 mL of THF, ~1:2  $\text{H}_2/\text{N}_2\text{O}$  (3 atm). After three successive 24 h cycles, where average cumulative apparent TONs of 982, 2055 and 3261 were measured, a total of 16.3 M of water was produced.

In summary, we have discovered “hidden” heterogeneous catalysis in the hydrogenation of  $\text{N}_2\text{O}$  using a rhodium(i) hydride complex featuring a nominally robust phosphine-based pincer ligand. Although reaction with  $\text{N}_2\text{O}$  by O-atom insertion into the Rh–H bond is facile, the ensuing dearomatized rhodium(i) derivative is unstable and partial decomposition into catalytically active rhodium nanoparticles and PNP-*t*Bu oxide was observed during catalysis. Commercially available and bench stable  $[\text{Rh}(\text{COD})(\text{OH})_2]$  was identified as a more effective catalyst precursor, enabling the hydrogenation of  $\text{N}_2\text{O}$  with an apparent turnover number >3000 at RT. We encourage the possible formation of small quantities of catalytically active nanoparticles to be carefully assessed when using molecular catalysts for this reaction.

## Data availability

The data supporting this article have been included as part of the ESI.<sup>†</sup><sup>19</sup>

## Conflicts of interest

There are no conflicts to declare.

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