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Reduction of carbon dioxide and organic carbonyls by hydrosilanes catalysed by the perrhenate anion

Danny S. Morris,[a] Catherine Weetman,[a] Julian T. C. Wennmacher,[b] Mirza Cokoja,[b] Markus Drees,[b] Fritz E. Kühn,[b] and Jason B. Love[a]*

The simple perrhenate salt [[N(hexyl)4][ReO4]] acts as a catalyst for the reduction of organic carbonyls and carbon dioxide by primary and secondary hydrosilanes. In the case of CO2, this results in the formation of methanol equivalents via silylformate and silylacetal intermediates. Furthermore, the addition of alkylamines to the reaction mixture favours catalytic amine N-methylation over methanol production under certain conditions. DFT analysis of the mechanism of CO2 reduction shows that the perrhenate anion activates the silylhydride forming a hypervalent silicate transition state such that the CO2 can directly cleave a Si-H bond.

Results and Discussion

Reduction of carbon dioxide

Initially, the reaction between CO2 (2.5 bar), PhSiH3 (2.0 mmol), and pyridinium perrhenate 1 (2.0 mol %) at 80 °C in C6D6 in a Teflon-tapped NMR tube was monitored by 1H NMR spectroscopy. However, only 15 % consumption of hydrosilane is seen under these conditions after 16 h (Fig. S2 and S3, ESI). In contrast, when the reaction is carried out using the simple lipophilic quaternary ammonium salt [[N(hexyl)4][ReO4]] 2 (2.5 mol%) with PhSiH3 in C6D6 at 1 bar of CO2 and at 80 °C, complete consumption of the hydrosilane is observed in the 1H NMR spectrum after 12 h (Fig. S4) along with the formation of silylformate (3), bis(silyl)acetals (4) and silylated methanol (5) products (Table 1, entry 1). Negligible depletion of hydrosilane (< 3 %) is seen when the reaction is carried out in the absence of CO2 (under air) for 1 h (Fig. S5 and S6), confirming that CO2 is
The choice of hydrosilane is important to the reaction as EtSiH (Table 1, entries 7) showed no conversion after 24 h at 80 °C, whereas (EtO)2SiH (Table 1, entry 9) is highly selective towards the formation of silylformate, and the use of more sterically demanding Ph3SiH (Table 1, entry 12) required elevated temperatures. This variation in reactivity is due to a combination of steric inaccessibility of the Si-H bond and the lower Lewis acidity of alkyl silanes.

Further solvent screening found the catalysis to be accelerated in pyridine, with complete hydrosilane consumption observed after 1.5 h (Table 1, Entry 9). Using d3-DMF accelerates the reaction further, with complete hydrosilane depletion after 1 h and an increase in selectivity towards methanol formation compared to the reaction carried out in pyridine (Table 1, entries 10 vs 11). Significantly however, reactions in DMF suffer from competitive solvent reduction by hydrosilane to (CD3)2NCDH2, consuming ca. 10% of the hydrosilane in this process (Fig. S21). The variation of solvent relates to an increase in turnover frequencies (TOFs), determined from the time taken to consume the hydrosilane at 80 °C, of 3.3 h−1 for C6D6 to 40 h−1 for d3-DMF. The increase in rate is, in part, due to the increased solubility of CO2 in the more polar solvent; indeed, a reaction carried out in CD3CN under 2 bar of CO2 shows complete hydrosilane depletion within 1.5 h (Fig. S22).

The longevity of the catalyst system was probed, and at the end of the first catalytic run with Ph3SiH in d3-DMF (TOF 40 h−1), the NMR tube was recharged with Ph3SiH3 and 1 bar of CO2 and heated again at 80 °C; this procedure was repeated 3 times. A marginal drop in TOF is observed on the third recharge cycle (36 h−1) after which the reaction was quenched with water and selective formation of methanol is seen (ratio 1:0:99, Fig S23). Whilst only a small drop in activity was noted after subsequent recharges, the perrhenate catalyst has significant advantages over current reports due to the ease in which the perrhenate anion can be recovered through simple reverse-phase-transfer techniques.

The faster rate of the reaction in d3-DMF allowed it’s monitoring by 1H and 13C NMR spectroscopy at 300 K using 13CO2. On depletion of hydrosilane, broad resonances are seen after 3 h consistent with the formation of silylformate 3 at 8.65 ppm (d, JdH 219 Hz) and 162.6 ppm (d, JCH 219 Hz) in the 1H and 13C NMR spectra, respectively (Fig. S24-29). After 5 h, quartet resonances at 51.9 ppm (JCH 144 Hz) appear in the 13C NMR spectrum, consistent with [Si]OCH3 5 formation, along with some small triplet resonances at 82.8 ppm (JCH 171 Hz) for the bis(silyl)acetal [Si]OCH3Si 4. In d3-DMF, the reaction between Ph3SiH2 and CO2 in the absence of perrhenate catalyst also leads to silylformate and silylether reduction products in a ratio of 38:62. However, this background reaction is very slow, taking 144 h to consume the Ph3SiH2 at 300 K compared with 1 h when using perrhenate (Fig. S30).

A series of stoichiometric reactions were undertaken to probe the catalytic mechanism. It was first thought that the mechanism may follow a similar route to the molybdate dianion which reacts initially with CO2 to form the carbonate complex Mo(CO3)2−,56 however, no reaction of 2 with 13CO2 in the absence of hydrosilane is seen, even after prolonged heating at 80 °C (Fig. S31), thus ruling out initial carbonate formation in this catalytic cycle. Also, no intermediates are seen in stoichiometric reactions of 2 with varying equivalents of hydrosilane in the absence of CO2. It is of note, however, that upon extended
heating (>16 hrs at 80 °C) decomposition of 2 occurs to form trihexylamine, siloxanes and a brown precipitate containing rhenium oxide clusters (Fig S32-34). In light of these experiments, the mechanism of this reaction was evaluated computationally.

**DFT modelling of the catalytic mechanism**

To explain how the carbon dioxide reacts with the hydro silane and the perrhenate catalyst, three different principle pathways have been elucidated (Scheme 2).

**Scheme 2.** The pathways considered for the DFT investigation of the reduction of CO$_2$ by hydro silanes catalysed by the perrhenate salt 2.

Two pathways include activation of the H-Si bond of the relevant hydro silane by either a [3+2] or [2+2] cycloaddition to the Re=O or O=Re=O fragment of the perrhenate to form a siloxyhydride, with subsequent reaction of this intermediate with CO$_2$ by hydride migratory insertion.$^{63, 65}$ If Si-H activation would occur to form a hydride, then the most probable mode would be [2+2] addition. However, the DFT results favour an alternative ΔG energy profile in the gas phase (Figure 1) which includes the formation of a simple complex of the hydro silane with perrhenate without preliminary Si-H activation, forming a five-coordinate hypervalent silicon centre.$^{2, 60, 67-70}$ The CO$_2$ activation occurs then directly at a Si-H bond to form a HCO$_2$ species that adds to the silicon to form the observed silylformate (here as adduct of ReO$_4$). This adduct can be seen as a starting point of activating the next Si-H bond by a second CO$_2$. In principle, CO$_2$ can also undergo a cycloaddition to silyl perrhenate intermediates, but the barriers are higher in all pathways. Calculations incorporating a solvent continuum were carried out, with neither benzene nor DMF models significantly altering the preferred mechanism or its energies (see SI). Furthermore, alternative mechanisms involving the cycloaddition or CO$_2$ to a rhenium silicate intermediate were explored, but were found to have higher energy barriers than the route described above (see SI).

**Figure 1.** Calculated Gibbs free-energy profile of the three different pathways

**N-methylation of amines using carbon dioxide**

The observation that silylformates are formed during the catalytic reaction and their implication as intermediates in the N-methylation of amines using CO$_2$ led us to assess the use of 2 to catalyse this latter reaction. Accordingly, the reaction between CO$_2$, HN$_2$Pr$_2$, 4 eq. of Ph$_2$SiH$_2$, and 2.5 mol% of 2 at 80 °C in CD$_3$CN was monitored by $^1$H NMR spectroscopy. After 2 h, complete loss of HN$_2$Pr$_2$ is observed with the concomitant formation of MeN$_2$Pr (5) as noted by the characteristic resonances in the $^1$H NMR spectrum between 3.4-3.6 ppm. The excess hydro silane is then consumed in the formation of [Si]OCH$_3$ (5) as noted by the characteristic resonances in the $^1$H NMR spectrum between 3.4-3.6 ppm. The scope of the amine substrate was evaluated, revealing that several aliphatic amines are N-methylated, including isopropylamine (to form Me$_2$NPr), piperidine, pyrrolidine and morpholine (Table 2, entries 2-5). The N-methylation of aromatic primary or secondary amines at this temperature does not occur (Table 2, entries 6 and 7), and instead the hydro silane is consumed in...
competitive CO₂ reduction. However, lowering the temperature of reaction negates the further reduction of silylformate by hydrosilane to favour reaction with the poorly nucleophilic N-methylaniline and, after 100 h at 20 °C, its conversion to N,N-dimethylaniline was seen in 40 % yield. Interestingly, the major product of this reaction is the aminal CH₂(NMePh₂), in 60 % yield, seen by its characteristic resonances at 2.86 and 4.78 ppm in the 1H NMR spectrum. Similar aminal formation from CO₂ has been seen previously in organocatalysed or Ru-catalysed reactions.47, 54 As the aminal can be prepared by the condensation reaction of N-methylaniline and formaldehyde, its formation in this catalysed reaction is likely a result of transient formaldehyde production which can arise from the decomposition of CH₂(OH)₂SiH₂.71

Table 2. N-methylation of amines using 2 bar CO₂ and Ph₂SiH₃ in CD₂CN, heated at 80 °C for 2 h with 2.5 mol% [N(hexyl)][ReO₄].

| Amine          | Hydrosilane (eq) | NMR yield (%) | TOF (h⁻¹) |
|----------------|------------------|---------------|-----------|
| 1 Diallylamine  | 4                | 99            | 19.8      |
| 2 Isopropylamine| 8                | 43³           | 8.6       |
| 3 Piperidine    | 4                | 87            | 17.4      |
| 4 Pyrrolidine   | 4                | 82            | 16.4      |
| 5 Morpholine    | 4                | 85            | 17        |
| 6 Aniline       | 8                | 0             | 0         |
| 7 N-methylaniline| 4               | 0             | 0         |
| 8 N-methylaniline| 4               | 40            | 0.4       |

³ NMR yield vs. Me₃SiPh; ⁴ Me₃NPr; ⁵ H₂SiPh, 20 °C, 100 h

It was reported recently that selective formylation of amines is possible using hydrosilanes and CO₂ in polar solvents such as DMF and DMSO.72 In our case, it was found that the simple aliphatic amine HNPr₂ underwent N-methylation in DMF at room temperature in the absence of 2, and subsequent in-situ monitoring of this reaction by 1H NMR spectroscopy found the initial rates essentially identical for the catalysed and uncatalysed reaction (Fig S40). Reactions in DMF for the other amine substrates are also selective towards N-formylation, which was possible in the absence of 2; however, to achieve N-methylation catalyst 2 was required.

Reduction of aldehydes and ketones

Following on from the success of the CO₂ reduction, attention was turned to C=O reduction for a variety of carbonyl containing substrates.73-75 An initial trial NMR reaction with benzaldehyde was carried out using the standard reaction conditions of 1.2 eq. of PhSiH₃, 0.5 mL of CD₂CN and 2.5 mol% of 2 at 80 °C. After 1 h, the 1H NMR spectrum showed near complete consumption of the aldehyde through loss of the characteristic CHO resonance at 10.01 ppm and formation of approximately a 50:50 mixture of PhSi(H)(OCH₂Ph₂) and PhSi(OCH₂Ph)₃; subsequent heating for a further 30 minutes to ensure full consumption of benzaldehyde resulted in no change to the product distribution. Simple hydrolysis through the addition of a small excess of water resulted in full conversion to the benzylalcohol product with concomitant formation of siloxanes (Fig S42). Following the same reaction protocol the substrate scope was expanded to other substituted arylaldehydes and alkylaldehydes (Table 3).

The arylaldehyde substrates provided efficient turnover to the corresponding benzylalcohol product upon quenching with water. Aryl substituents containing electron-withdrawing groups (Table 3, entry 2 and 5) proceed with higher TOFs compared to their electron-donating counterparts (Table 3, entry 3 and 4), in line with previous reports of rhenium catalysed hydrosilylation reactions of aldehydes.76 In contrast the alkylaldehydes containing more sterically demanding substituents require twice the reaction time in comparison with the linear butyl chain derivatives.

Table 3. Hydroisilylation of aldehydes using 1.2 eq. PhSiH₃ in CD₂CN at 80 °C with 2.5 mol% [N(hexyl)][ReO₄].

| Aldehyde          | Time (h) | NMR yield (%) | TOF (h⁻¹) |
|--------------------|----------|---------------|-----------|
| 1 Benzaldehyde     | 1.5      | 86            | 22.9      |
| 2 p-Bromobenzaldehyde| 1       | 92            | 36.8      |
| 3 p-Toluinaldehyde | 2.5      | 79            | 12.6      |
| 4 p-Anisaldehyde   | 2.5      | 89            | 14.2      |
| 5 m-Anisaldehyde   | 1.5      | 96            | 25.6      |
| 6 Trimethylacetaldehyde| 4   | 91            | 2.3       |
| 7 (1R)-(−)-Myrtanyl| 4        | 47            | 3.7       |
| 8 Crotonaldehyde   | 2.5      | 48            | 7.7       |
| 9 Butyraldehyde    | 2        | 46            | 9.2       |

³ NMR ratio vs. Me₃SiPh after water quench; ⁴ TOF = (conversion/catalyst loading)/time

Further extension of this Perrhenate hydrosilylation catalysis examined the reduction of ketones. Using the same reaction protocol with acetonophene, and monitoring by 1H NMR spectroscopy, the loss of the singlet resonance for the CH₃ protons at 2.56 ppm is seen after 21 h at 80 °C with three new doublet resonances appearing in the range 1.49 – 1.37 ppm that correspond to oligomeric PhCH₂(O-[Si])CH₃ products; upon quenching with water these resonances resolve into a single species at 1.42 ppm (Δν = 6.51 Hz). The same is also true for the CH(O-[Si])CH₃ proton, visible around 5.1 ppm, but due to the oligomeric nature of the silylether products and the overlapping remaining [Si]-H resonances this appears as a series of multiplets which resolve into the characteristic quartet at 4.85 ppm (Δν = 6.39 Hz) on quenching. Expanding the scope of this ketone reduction to include substituted acetophenones follows the same trend as observed with the benzaldehyde derivatives. In this case, however, prolonged reaction times are required for the electron-donating substituents, taking 40 h for only 50%
consumption of the starting ketone (Table 4, entries 2 and 4 vs 3 and 5). Reduction of benzophenone to the corresponding alcohol proceeds efficiently, and again the use of a more sterically demanding alkyl ketone requires prolonged reaction times. Interestingly, a small amount of H/D exchange was seen to take place during extended heating. Hydrogenation occurs during the initial stages of the reaction where some of the hydrosilane is initially consumed in the reduction of trace water to form H₂ and siloxanes and, in the case of the acetophenone, HD is seen in the 1H NMR spectrum as a characteristic 1:1:1 triplet at 4.56 ppm (J_HD_ = 42.6 Hz) (Fig S558). Further H/D exchange was seen at the acetyl position of the acetophenone substrates and is thought to occur through ketenol tautomerisation in the presence of the [Si]-D which results from the reaction of [Si]:H and D₂O. The use of dry d-solvents negates this HD exchange.

Table 4. Hydrosilylation of ketones using 1.2 eq. PhSiH₂ in CD₂CN at 80 °C with 2.5 mol% [N(hexyl)₄][ReO₄].

| Ketone           | Time (hr) | NMR yield (%) | TOF (h⁻¹) |
|------------------|-----------|---------------|-----------|
| Acetophenone     | 21        | 72            | 1.4       |
| p-Bromoacetophenone | 40        | 45            | 0.5       |
| p-acetyltoluene  | 21        | 66            | 1.3       |
| p-Acetanisole    | 40        | 39            | 0.4       |
| m-Acetanisole    | 20        | 81            | 1.6       |
| Benzophenone     | 21        | 66            | 1.3       |
| Pinacolone       | 37        | 22            | 0.24      |

Experimental

Synthesis of [N(hexyl)₄][ReO₄]. 2. An aqueous solution of ammonium perrhenate (1.26 g, 4.7 mmol) was added to a chloroform solution of tetrahexylammonium bromide (2.00 g, 4.6 mmol) and stirred together for 6 hours at room temperature after which the two layers were separated and the aqueous layer extracted with chloroform (2 x 10 mL). The combined chloroform extracts were dried over magnesium sulphate and the solvent removed under reduced pressure to provide a colourless solid of tetrahexylammonium perrhenate (2.10 g, 75 % yield).

1H NMR (500 MHz; d₆-MeCN, 300 K): δ_H (ppm) 3.07 (m, 8H, CH₂), 1.33 (m, 24H, CH₃), 0.91 (t, 12H, CH₃). 13C NMR (500 MHz; d₆-MeCN, 300 K): δ_C (ppm) 59.48 (NCH₂), 31.84 (CH₂), 26.57 (CH₃), 26.57 (CH₂), 23.10 (CH₃), 22.34 (CH₂), 14.21 (CH₃); FTIR (ATR): ν_max/cm⁻¹: 902 (Re=O); ESI-MS: M⁺ m/z found: (calculated): 354.41068 (354.40943 C₆H₂N₂), 959.77918 (959.75512 (C₂H₅N₂)ReO₄), 1565.16124 (1565.10132 (C₂H₅N₂)ReO₄). M⁺ m/z found (calculated): 250.93270 (250.93597 ReO₄), 854.26749 (854.27860 (C₂H₅N₂)ReO₄), 1459.59185 (1459.62427 (C₂H₅N₂)ReO₄), 2064.90770 (2064.97026 (C₂H₅N₂)ReO₄). Analysis: C₂H₅O₄Re found (calc.); C: 47.55 % (47.65), H: 8.72 % (8.67), N: 2.38 % (2.32).

General Procedure for catalytic reactions of hydrosilanes with CO₂

[N(hexyl)₄][ReO₄] 2 (3 mg, 2.5 mol %) in 0.6 mL d-solvent, hydrosilane (0.2 mmol) and trimethylphenylsilane (2 µL) as an internal standard (unless otherwise stated) were added to a Teflon-tapped NMR tube. The solution was freeze-pump-thaw degassed three times before being refilled with 1 bar of CO₂. The 1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C). The reactions were monitored by 1H NMR spectroscopy regularly until the hydrosilane was consumed. At this point the reaction was quenched with water (10 µL, 0.56 mmol), heated for 2 h and the 1H NMR spectrum recorded.

General Procedure for catalytic N-methylation of amines with CO₂

[N(hexyl)₄][ReO₄] 2 (3 mg, 2.5 mol %) in 0.6 mL d-solvent, amine (0.2 mmol), silane (0.8 mmol) and trimethylphenylsilane (2 µL) as an internal standard (unless otherwise stated) were added to a Teflon-tapped NMR tube. The solution was freeze-pump-thaw degassed three times before being refilled with 2 bar of CO₂. The 1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C) for 2 h, after which the 1H NMR spectrum was recorded.

General Procedure for catalytic hydrosilylation of aldehydes and ketones

[N(hexyl)₄][ReO₄] 2 (3 mg, 2.5 mol %) in 0.5 mL CD₂CN, phenylsilane (0.24 mmol), carbonyl (0.2 mmol) and trimethylphenylsilane (2 µL) as an internal standard were added to a NMR tube. The 1H NMR spectrum was recorded and then the tube was placed in a preheated oil bath (80 °C). The reactions were monitored by 1H NMR spectroscopy regularly until the hydrosilane or carbonyl was consumed. At this point the reaction was quenched with water (10 µL, 0.56 mmol), heated for 15 min and the 1H NMR spectrum recorded.

Computational Details

All calculations have been performed with the software Gaussian09. The hybrid density functional B3LYP 76-81 has been used together with dispersion correction GD3BJ 82 and the triple zeta basis set 6-311++G** 83,84 for all elements except Re. The Re atoms are described with the Stuttgart-Dresden-ECP. 85 The energies reported are free energies in gas-phase or for the solvents benzene and DMF with SMD solvent calculations at 298.15 K. 86

Conclusions

We have shown that the simple, lipophilic perrhenate salt [N(hexyl)₄][ReO₄] acts as a catalyst for the reduction of CO₂ by hydrosilanes. This is the first time that perrhenate has acted as a catalyst for CO₂ reduction, and is likely facilitated by dissolution of the lipophilic assembly into a hydrophobic.
organic solvent. The calculated mechanism shows that direct attack of CO$_2$ on a Si-H bond of a perrhenate hypervalent silicate occurs instead of alternative mechanisms through rhenium hydride formation. Furthermore, the observation that N-methylation of amines using CO$_2$ and organic carbonyl reduction can also be undertaken using a perrhenate catalyst expands considerably the scope of this chemistry. The ease of transfer of perrhenate from an organic phase back into an aqueous phase by the addition of base (e.g. NaOH) should lead to straightforward rhenium recycling, an essential step if this precious metal is to be further exploited in catalytic chemistry.

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