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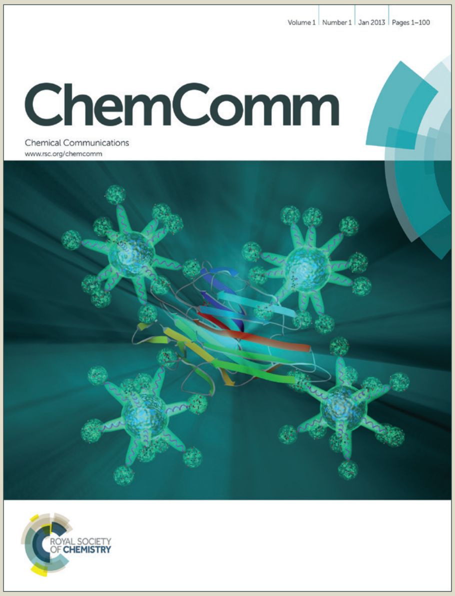

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Trapping Atmospheric CO_2 with Gold

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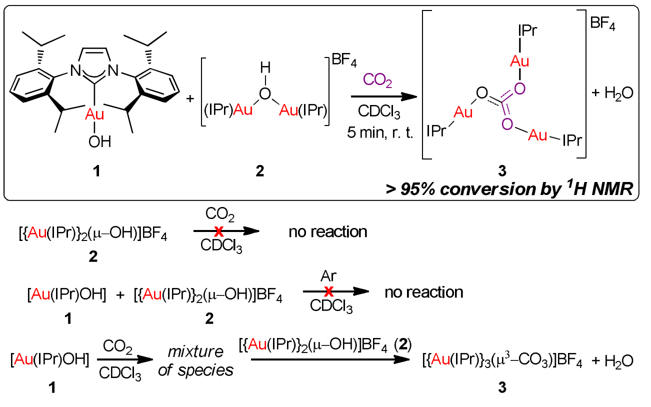
The ability of gold-hydroxides to fix CO_2 is reported. [Au(IPr)(OH)] and [{Au(IPr)}$_2$(μ-OH)][BF_4] react with atmospheric CO_2 to form the trigold carbonate complex [{Au(IPr)}$_3$(μ^3-CO_3)][BF_4]. Reactivity studies revealed that this complex behaves as two basic and one cationic Au centers, and that it is catalytically active. DFT calculations and kinetic experiments have been carried out.

CO_2 storage and functionalization are two key challenges in modern chemistry.[1] CO_2 is an attractive feedstock as it is abundant, cheap, and relatively non-toxic.[2] The main obstacles to developing its use as a C1 building block are its high thermodynamic and kinetic stability. One way to overcome this issue is by activation with transition metal (TM) complexes.[3] In this context, much effort is being devoted to the study of the behavior of CO_2 in the coordination sphere of TM complexes. Of particular interest are the reactions between M-OH species and CO_2, as they are involved in enzymatic transformations. The reactive form of carbonic anhydrases contain Zn-OH motifs that catalyze the conversion of CO_2 to bicarbonate and *vice versa*.[4] Several examples of the insertion of CO_2 into M-OH bonds to give carbonate or bicarbonate species have been reported with Co,[5] Ir,[6] Cu,[7] Ni,[8] Pt[9], and Zn,[5, 7c, 10] among others. To the best of our knowledge, the stoichiometric reactions of Au-OH complexes with CO_2 have never been reported.

One of our research interest is the synthesis and reactivity of new Au species bearing *N*-heterocyclic carbene (NHC) ligands.[11] We have recently reported the preparation of monogold-NHC[12] and digold-NHC hydroxide complexes.[13] These compounds have proven to be powerful synthons capable of activating a variety of bonds under mild conditions[12b, 14] and efficient catalysts in numerous transformations.[15] Serendipity drew our attention to the reactivity of Au-OH complexes with CO_2. Indeed, when attempting to crystallise different [Au(NHC)(OH)] species, the solid-state structures obtained were not always the simple ones expected and preliminary structural data revealed higher nuclearity species being formed containing a carbonate moiety. The crystallisation solutions were prepared under air and, presumably, the carbonate complexes were formed by reaction of the Au-OH derivatives with atmospheric CO_2. Intrigued by these results, we explored the reactivity of well-defined [Au(IPr)(OH)] (**1**) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (**2**) with CO_2.

A mixture of complexes was obtained when a solution of **1** was exposed to CO_2, and no reaction was observed when **2** was placed under one atmosphere of CO_2 (Scheme 1). However, when a $CDCl_3$ solution containing equimolar amounts of **1** and **2** was exposed to CO_2, full conversion to a single complex was obtained after 5 min at r.t. This species was characterized as the trigold carbonate complex, [{Au(IPr)}$_3$(μ^3-CO_3)][BF_4] (**3**).[16] No reaction was observed between **1** and **2** under argon. We reasoned that the first step of the transformation must involve **1** and CO_2. In fact, the mixture initially obtained in this reaction is readily transformed into **3** when 1 equiv of **2** is added (Scheme 1).



Scheme 1. Reactions of [Au(OH)(IPr)] (**1**) and [{Au(IPr)}$_2$(μ-OH)][BF_4] (**2**) with CO_2

Complex **3** was fully characterized by ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectroscopies. The ^{1}H NMR spectrum shows a simple pattern for the IPr moiety, suggesting a highly symmetrical structure. Accordingly, the $^{13}C\{^{1}H\}$ NMR spectrum shows one signal, at 166.4 ppm, corresponding to the carbenic carbon atoms. The carbonate carbon atom resonates at 169.2 ppm. The incorporation of CO_2 in the molecule was further confirmed by conducting the reaction under $^{13}CO_2$.[17] The structure of **3** was unambiguously confirmed by X-ray diffraction analysis (Fig 1).[18] Two molecules were found in the crystal lattice, where the CO_3 units are planar. The C-O distances lie in the range 1.20(3)-1.31(2) Å.[16,19] The Au-O distances are in the range 2.025(16)-2.089(16) Å. The Au_3CO_3 core presents approximate C_3 symmetry.

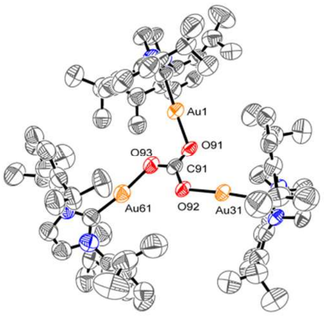


Fig 1. Thermal ellipsoid at 50 % probability of one of the two molecules found in the crystal lattice of 3. H atoms and BF_4 omitted for clarity. Selected bond lengths (Å) and angles (º): Au1-O91 2.081(14), Au31-O92 2.054(14), Au61-O93 2.089(16), O91-C91 1.20(3), O92-C91 1.31(2), O93 C91 1.26(3), O91-C91-O92 119.7(19), O91-C91-O93 121.7(18), O92-C91-O93 118.5(19).

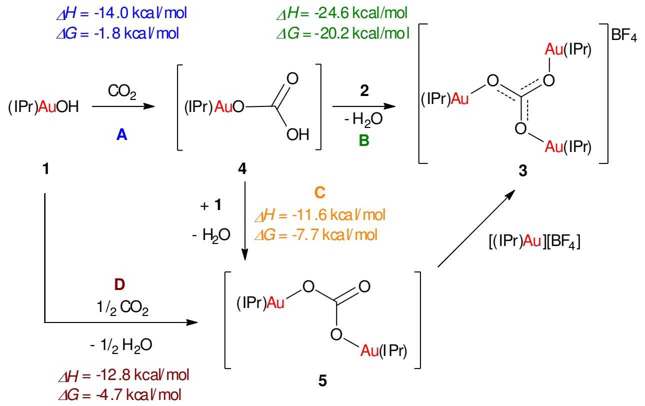
Analysis of this structure was performed computationally (optimization) at the PBE0/ECP1 level and natural population analysis was performed at the PBE0/ECP2/PCM level.[20] The minimum obtained is in agreement with the crystal structure, (planar CO_3 center and almost local C3 symmetry at the Au_3CO_3 core). The C-O distances are 1.285-1.287 Å and the Au-O distances are 2.062-2.067 Å. The electrostatic potential showed that the carbon atom of the CO_3 moiety has the highest positive charge (+1.0 *e*) followed by the Au centers (+0.40 *e*, on each Au). However, these atoms are shielded by the O atoms (where the most negative charge is localized, -0.80 *e* on each O atom) and the most positive area in the complex appears to be the backbone of the NHCs.[17]

Although full conversion to **3** is observed when using bench solvents, attempts to isolate it under non anhydrous conditions afforded a mixture of starting materials and product. Interestingly, the obtained mixture could be converted again into **3** by dissolving it in CH_2Cl_2 and exposing it to CO_2. This observation suggests that CO_2 capture by the Au-hydroxides is a reversible process. The isolation of **3** in high yield was achieved when dry solvents were used and 4 Å molecular sieves were added to the reaction medium in order to trap the generated water. Complex **3** was isolated as a white solid in 76 % yield and further characterised by elemental analysis and solid-state IR spectroscopy. The IR spectrum shows a band at 1433 cm^{-1} corresponding to the C-O stretching frequency of the CO_3 unit. This band supports the $M_3(\mu^3\text{-}CO_3)$ coordination mode.[7a, 16, 19]

The ease with which these complexes trap CO_2 encouraged us to explore the reaction using air as a CO_2 source. **1** and **2** were dissolved in dry CH_2Cl_2, and compressed air was bubbled through the solution for 20 min. Gratifyingly, ^{1}H NMR analysis of the solution showed 75 % conversion to **3**, reflecting the ability of the Au-hydroxides to react selectively with CO_2 from air and convert it into a carbonate unit (eq. 1). Importantly, the formation of **3** was also observed when a solution of **1** and **2** was stirred in an open vial for several hours. Although other metals are known to trap atmospheric CO_2,[7a, 21] to the best of our knowledge this is the first example of atmospheric CO_2 fixation with Au complexes.

$$\underset{\mathbf{1}}{[Au(IPr)OH]} + \underset{\mathbf{2}}{[\{Au(IPr)\}_2(\mu\text{-}OH)]BF_4} \xrightleftharpoons{air} \underset{\mathbf{3}}{[\{Au(IPr)\}_3(\mu^3\text{-}CO_3)]BF_4} + H_2O \quad (eq\ 1)$$

Based on the experimental observations, we propose the following mechanism. First, **1** would react with CO_2 to form the bicarbonate product **4**, as has been shown with other M-OH complexes.[1a] In the absence of **2**, **4** could react with another molecule of **1** to afford the digold carbonate species **5**,[5-6] which would explain the mixture of complexes obtained when [Au(OH)(IPr)] is reacted with CO_2. When **2** is present, **3** is formed as a single species. We have postulated that **2** can dissociate in solution into [Au(IPr)(OH)] and $[Au(IPr)][BF_4]$.[15b] Then, the Au-OH unit would react with **4**, affording **5** that would finally be trapped by the cationic Au fragment to yield **3** (Scheme 2).



Scheme 2. Single steps of the proposed mechanism evaluated computationally.

To gain insight into the driving force leading to **3** the proposed single steps were evaluated computationally.[20] The reaction of **1** with CO_2 to afford the bicarbonate **4** and its subsequent reaction with **2** to give **3** (Scheme 2, A and B) are computed to be strongly exothermic and noticeably exergonic at r.t., which is consistent with the efficient production of **3** from **1** and **2**. The intermediate **4** has a strong driving force to react with **1** to form the neutral digold carbonate **5** (Scheme 2, C). The overall driving force for the formation of the latter from one equivalent of **1** is shown in Scheme 2, D.

As the reaction between **1** and $[Au(IPr)(NTf_2)]$ (**6**) is known to deliver **2**,[13] the formation of **3** using monogold species was attempted. **3'**, with a NTf_2 counterion, was obtained by placing **6** and two equiv. of **1** under CO_2 (eq 2).

$$\underset{\mathbf{1}}{2\,[\mathrm{Au(IPr)OH}]} + \underset{\mathbf{6}}{[\mathrm{Au(IPr)(NTf_2)}]} \xrightarrow[\mathrm{CDCl_3}]{\mathrm{CO_2}} \underset{\mathbf{3'}}{[\{\mathrm{Au(IPr)}\}_3(\mu^3\text{–}\mathrm{CO_3})]\mathrm{NTf_2}} + \mathrm{H_2O} \quad \text{(eq 2)}$$

The preparation of analogues of **3** bearing two or three different NHC ligands using a) [Au(OH)(SIPr)] and $[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ or b) [Au(OH)(IPr)], [Au(OH)(SIPr)], and $[Au(NTf_2)(IPr^{Cl})]$ in the presence of $^{13}CO_2$ was attempted. Unfortunately, a mixture of trigold carbonates was always obtained.[17] Nevertheless, this scrambling supports the proposed mechanism. If two different Au-OH species are present in solution (either as starting material or as a result of the dissociation of **2**), both could react with CO_2 to give two bicarbonate species. They would react again with the hydroxides to afford a mixture of digold carbonate species, and therefore, a single carbonate final product would not be obtained.

To gain further insight into the formation of **3**, kinetic studies following the reaction by solution infrared (IR) spectrometry were carried out. Complexes **1** and **2** were dissolved in dry CH_2Cl_2 under N_2 and were placed in a purpose-built continuously stirred tank reactor (CSTR) fitted with spectroscopic windows. The CSTR was then pressurized with CO_2 during the collection of a series of IR spectra.[17] The progress of the reaction was monitored by the disappearance of the band corresponding to the combination of the O-H vibrations of both starting materials (Fig. 2). Notably, **1** and **2** were consumed after only 4 min at 22 ºC. Full conversion to **3** was further confirmed by ^1H NMR analysis of the solution.

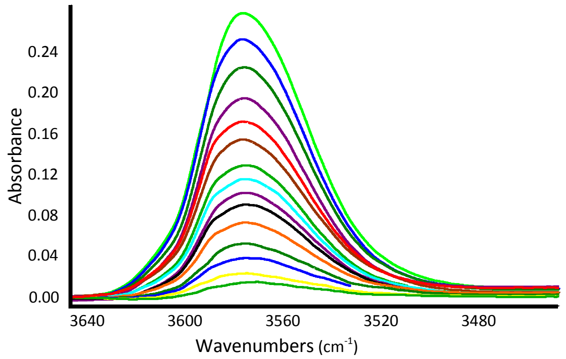
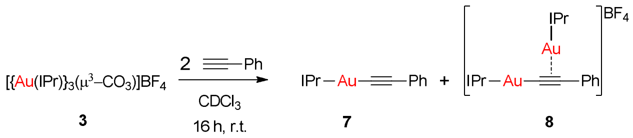


Fig 2. Disappearance of the $\upsilon_{O\text{-}H}$ band associated to **1** and **2** in the presence of CO_2 over time.

The experiment was carried out at 4 different temperatures (22.0, 14.5, -0.3, and -12.3 ºC). The obtained kinetic traces were fitted to pseudo first order exponentials and the activation parameters of the process were obtained applying the Eyring-Polanyi equation.[17] The calculated parameters show a low activation barrier, $\Delta H^\ddagger = 8 \pm 3$ kcal/mol, and a negative activation entropy $\Delta S^\ddagger = -27 \pm 11$ e.u., suggesting an associative transition state. The activation free energy was calculated at 298 K: $\Delta G^\ddagger{}_{298} = 17 \pm 4$ kcal/mol, which is in agreement with a facile process at r.t.

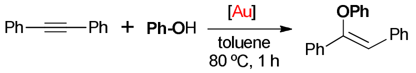
To gain insight into the behavior of the Au centers in **3**, we explored its stoichiometric reactivity towards a terminal alkyne, as this is a well-known reaction with Au species. Treatment of **3** with 2 equiv of phenylacetylene afforded two species that were identified as the gold-acetylide (**7**) and the digold-σ,π-acetylide complexes (**8**) (Scheme 3).[12b, 14a, 17] The former species is the product of the reaction of a basic Au complex, such as [Au(IPr)(OH)],[12b] with a terminal alkyne, while the latter species is the result of reacting a basic Au-OH complex and a cationic Au species, e.g. $[Au(IPr)(CH_3CN)]^+$, with a terminal alkyne.[14a] Therefore, the outcome of this reaction suggests that **3** behaves as two basic and one cationic Au centers.



Scheme 3. Stoichiometric reactivity of **3** with phenylacetylene

In an effort to determine whether **3** was catalytically active or a catalytic dead-end, its activity was tested in the hydrophenoxylation of diphenylacetylene (Table 1). We have recently shown that digold hydroxide species are efficient catalysts in this transformation.[15a] To make all entries comparable, the overall Au concentration was kept constant at 1 mol % in each case. The reported conditions, using **2** as the catalyst, are shown in entry 1. [15a]

Table 1. Catalytic behavior of **3** in the hydrophenoxylation of PhC≡CPh[a]



Entry	Catalyst	Conditions	Conversion (%)[b]
1	$[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ **2**	air	96[14a]
2	$[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ **2**	CO_2	99
3	$[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ **2** + [Au(OH)(IPr)] **1**	air	92
4	$[\{Au(IPr)\}_2(\mu\text{-}OH)][BF_4]$ **2** + [Au(OH)(IPr)] **1**	CO_2	96
5	$[\{Au(IPr)\}_3(\mu^3\text{-}CO_3)][BF_4]$ **3**	air	91
6	$[\{Au(IPr)\}_3(\mu^3\text{-}CO_3)][BF_4]$ **3**	CO_2	90

[a]Au (1 mol%), PhC≡CPh (0.50 mmol, 1 equiv.), phenol (0.55 mmol, 1.1 equiv.), toluene (1.0 mL), 80 ºC. [b] GC conversion, average of two runs.

The effect of CO_2 in this transformation was investigated by conducting the reaction under CO_2 atmosphere. The incorporation of CO_2 was not observed and the hydrophenoxylation product was obtained in similar GC conversions (entries 1 and 2). Next, the catalytic activity of equimolar amounts of **1** and **2** was tested in air, where significant conversion to **3** is not expected (entry 3);[22] and under CO_2 where **3** is formed *in situ* (entry 4). The desired product was obtained in 92 and 96% conversions, respectively. Finally, the well-defined trigold species **3** was tested in air (entry 5) and CO_2 (entry 6), leading to conversions of 91 and 90% of product, respectively. In all cases the conversions obtained were comparable which indicates that **3** is catalytically active. This observation along with its ease of formation in air suggests that **3** may very well represent a possible catalyst resting state in Au-NHC catalysis.

Conclusions

In conclusion, [Au(IPr)(OH)] (**1**) and [{Au(IPr)}$_2$(μ-OH)][BF$_4$] (**2**) are able to trap atmospheric CO$_2$ to afford a carbonate trigold species [{Au(IPr)}$_3$(μ^3-CO$_3$)][BF$_4$] (**3**). The process is reversible and water plays a key role in the equilibrium. Reactivity studies have shown that **3** acts as two basic and one cationic Au units, and that it is catalytically active, suggesting that **3** is a possible catalyst resting-state. The driving force for the transformation has been theoretically calculated. Activation parameters have been obtained experimentally. Further studies focusing on the catalytic uses of **3** and functionalization of the carbonate unit are ongoing.

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Notes and references

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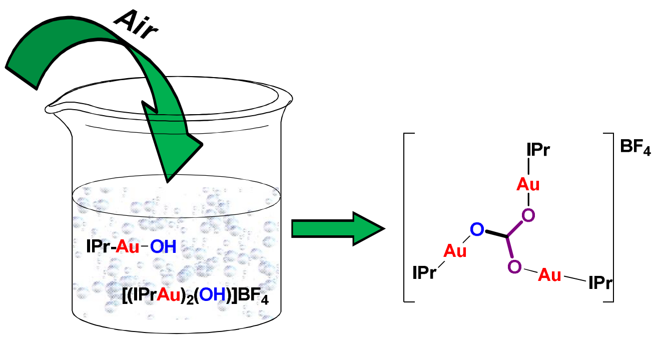
† IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIPr: 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; IPr^{Cl} : 4,5 dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

Electronic Supplementary Information (ESI) available: Experimental details, full characterization data, NMR spectra, DFT information, kinetic studies and crystallographic information. See DOI: 10.1039/c000000x/

1. a) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621-6658; b) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365-2387.
2. a) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.*, 2013, **114**, 1709-1742; b) Y. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, **48**, 9956-9964; c) D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765-10780; d) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975-2992.
3. a) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27-59; b) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063-2096.
4. H. Vahrenkamp, *Dalton Trans.*, 2007, 4751-4759.
5. C. Bergquist, T. Fillebeen, M. M. Morlok and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 6189-6199.
6. a) B. J. Truscott, D. J. Nelson, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2014, **50**, 286-288; b) D. W. Lee, C. M. Jensen and D. Morales-Morales, *Organometallics*, 2003, **22**, 4744-4749.
7. a) A. Company, J.-E. Jee, X. Ribas, J. M. Lopez-Valbuena, L. Gómez, M. Corbella, A. Llobet, J. Mahía, J. Benet-Buchholz, M. Costas and R. van Eldik, *Inorg. Chem.*, 2007, **46**, 9098-9110; b) J. Mukherjee, R. Gupta, T. Mallah and R. Mukherjee, *Inorg. Chim. Acta*, 2005, **358**, 2711-2717; c) C. Bazzicalupi, A. Bencini, A. Bencini, A. Bianchi, F. Corana, V. Fusi, C. Giorgi, P. Paoli, P. Paoletti, B. Valtancoli and C. Zanchini, *Inorg. Chem.*, 1996, **35**, 5540-5548.
8. a) M. Vogt, O. Rivada-Wheelaghan, M. A. Iron, G. Leitus, Y. Diskin-Posner, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Organometallics*, 2012, **32**, 300-308; b) D. Huang, O. V. Makhlynets, L. L. Tan, S. C. Lee, E. V. Rybak-Akimova and R. H. Holm, *Proc. Natl. Acad. Sci.*, 2011, **108**, 1222-1227; c) D. Huang and R. H. Holm, *J. Am. Chem. Soc.*, 2010, **132**, 4693-4701; d) T. J. Schmeier, A. Nova, N. Hazari and F. Maseras, *Chem. Eur. J.*, 2012, **18**, 6915-6927; e) O. Troeppner, D. Huang, R. H. Holm and I. Ivanovic-Burmazovic, *Dalton Trans.*, 2014, **43**, 5274-5279.
9. T. L. Lohr, W. E. Piers and M. Parvez, *Dalton Trans.*, 2013, **42**, 14742-14748.
10. a) W. Sattler and G. Parkin, *Polyhedron*, 2012, **32**, 41-48; b) W. Sattler and G. Parkin, *Chem. Sci.*, 2012, **3**, 2015-2019.
11. S. P. Nolan, *Acc. Chem. Res.*, 2011, **44**, 91-100.
12. a) S. R. Patrick, A. Gómez-Suárez, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2013, **33**, 421-424; b) S. Gaillard, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 2742-2744.
13. R. S. Ramón, S. Gaillard, A. Poater, L. Cavallo, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2011, **17**, 1238-1246.
14. a) A. Gómez-Suárez, S. Dupuy, A. M. Z. Slawin and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2013, **52**, 938-942; b) A. Collado, A. Gómez-Suárez, Y. Oonishi, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2013, **49**, 10745-10747.
15. a) Y. Oonishi, A. Gómez-Suárez, A. R. Martin and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2013, **52**, 9767-9771; b) S. Gaillard, J. Bosson, R. S. Ramón, P. Nun, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2010, **16**, 13729-13740.
16. An analogous trigold carbonate species with a OTf counterion has recently been obtained by treatment of [Au(OSiMe$_3$)(IPr)] and [Au(OTf)(IPr)] with CO$_2$. In contrast with our procedure, the reaction requires 72 h at 40 ºC. See: T. J. Robilotto, J. Bacsa, T. G. Gray, J. P. Sadighi, *Angew. Chem. Int. Ed*; **2012**, *51*, 12077-12080
17. See ESI
18. CCDC 1006986 (**3**) contain the supplementary crystallographic data. It can be obtained *via* http://www.ccdc.cam.ac.uk/data_request/cif.
19. a) S. Khan, S. Roy, K. Bhar, R. K. Kumar, T. K. Maji and B. K. Ghosh, *Polyhedron*, 2012, **32**, 54-59; b) W. Huang, P.-Y. Sun, J.-L. Fang, Y.-F. Sun and S.-H. Gou, *Transition Met. Chem.*, 2003, **28**, 925-929.
20. Computations performed at the PBE0-D3/SDD/6-311+G**(6-31G*)/PCM level for PBE0/SDD/6-31G*(*) optimised structures.
21. a) P. Bag, S. Dutta, P. Biswas, S. K. Maji, U. Florke and K. Nag, *Dalton Trans.*, 2012, **41**, 3414-3423; b) L.-Y. Kong, Z.-H. Zhang, H.-F. Zhu, H. Kawaguchi, T.-a. Okamura, M. Doi, Q. Chu, W.-Y. Sun and N. Ueyama, *Angew. Chem., Int. Ed.*, 2005, **44**, 4352-4355; c) R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313-315; d) N. Kitajima, S. Hikichi, M. Tanaka and Y. Morooka, *J. Am. Chem. Soc.*, 1993, **115**, 5496-5508; e) S. Jamali, D. Milic, R. Kia, Z. Mazloomi and H. Abdolahi, *Dalton Trans.*, 2011, **40**, 9362-9365; f) L. Du, S. Zhang and Y. Ding, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1039-1041.
22. The formation of **3** under air after short periods of time is only observed when air is bubbled through the solution.



Atmospheric CO_2 fixation