



UNIVERSITY OF LEEDS

This is a repository copy of *Observation of guanidine-carbon dioxide complexation in solution and its role in reaction of carbon dioxide and propargylamines*.

White Rose Research Online URL for this paper:

<http://eprints.whiterose.ac.uk/79472/>

Version: Accepted Version

---

**Article:**

Nicholls, R, Kaufhold, S and Nguyen, BN (2014) Observation of guanidine-carbon dioxide complexation in solution and its role in reaction of carbon dioxide and propargylamines. *Catalysis Science & Technology*, 4. pp. 3458-3462. ISSN 2044-4753

<https://doi.org/10.1039/C4CY00480A>

---

**Reuse**

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

## COMMUNICATION

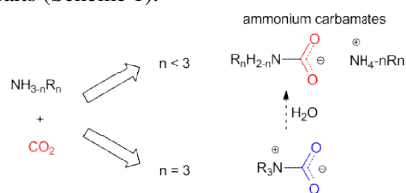
## Observation of Guanidine-Carbon Dioxide Complexation in Solution and Its Role in Reaction of Carbon Dioxide and Propargylamines

Rachel Nicholls,<sup>b</sup> Simon Kaufhold<sup>a</sup> and Bao N. Nguyen<sup>\*a, b</sup>Received 14th April 2014, Accepted 10<sup>th</sup> June 2014

DOI: 10.1039/c4cy00480a

The first observation of guanidine-CO<sub>2</sub> 'activation' complexes in solution using ATR-FTIR is reported. While cyclic guanidines TBD and MTBD form stable and detectable complexes with CO<sub>2</sub>, other guanidines and tertiary amines do not. Correlation with catalytic activity of these amines/guanidines in reaction between CO<sub>2</sub> and propargylamines indicated that the basicity of the catalyst, rather than its ability to form complexes with CO<sub>2</sub>, is the origin of catalytic activity.

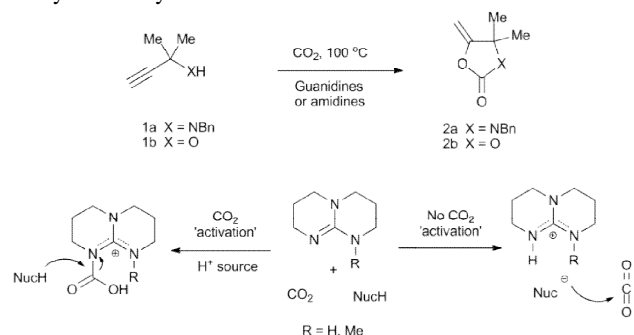
The thermodynamic stability of carbon dioxide (CO<sub>2</sub>),<sup>1</sup> is one of the main obstacles in developing practical processes to convert man made CO<sub>2</sub> into useful chemicals. However, facile reactions between organic bases and CO<sub>2</sub> to give carbonate and carbamate salts are well-known and have long been employed in CO<sub>2</sub> scrubbing,<sup>2</sup> and, more recently, switchable polarity solvents.<sup>3</sup> Although these are equilibria, they do not require high energy reactants to effect reactions with CO<sub>2</sub>. When trisubstituted amines are employed, the products are zwitterionic complexes instead of carbamate salts (Scheme 1).<sup>4</sup>

Scheme 1 Reactions between CO<sub>2</sub> and N-bases

Villiers isolated and characterized the first complexation product of this type between 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and CO<sub>2</sub> in the solid state,<sup>5</sup> and suggested that this could allow activation of CO<sub>2</sub> for catalytic conversion into high value chemicals.<sup>4, 6, 7</sup> Similar complexes have also been proposed by North and co-workers to explain improved catalytic activity in their cyclic carbonate production process in the presence of tributylamine.<sup>8</sup>

Guanidines, such as 7-methyl-1,5,7-triaza-bicyclo[4.4.0]dec-5-ene (MTBD), have been reported to catalyse reactions between CO<sub>2</sub> and propargylamines (Scheme 2).<sup>9</sup> The proposed mechanism involves deprotonation of the substrate by a superbases, i.e. the guanidine, rather than formation of a guanidine-CO<sub>2</sub> complex. Importantly, guanidines and amidines are both superbases and strong nucleophiles,<sup>10</sup> and the mechanisms outlined in Scheme 2 are equally probable. In addition, *ab initio*, DFT and MD

calculations have shown that both nucleophilicity and steric factors modulate complexation between amines and alkanolamines and CO<sub>2</sub>.<sup>11</sup> Consequently, the origin of the catalytic activity is difficult to delineate.

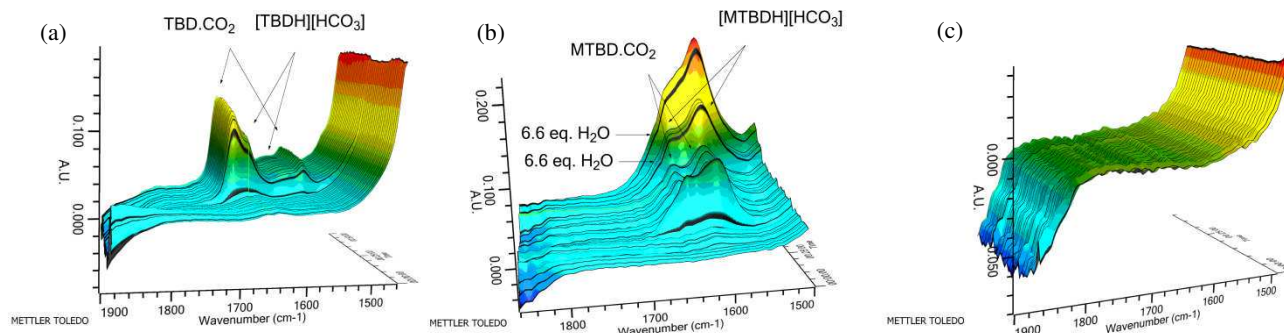
Scheme 2 Reaction between CO<sub>2</sub> and propargylamines and possible mechanisms with/without CO<sub>2</sub> 'activation'

Understanding 'CO<sub>2</sub> activation', particularly in catalytic context, is fundamental to sustainable CO<sub>2</sub> capture and utilisation processes.<sup>12</sup> Solid state NMR data on DBU.CO<sub>2</sub> and TBD.CO<sub>2</sub> complexes has been previously reported by Franco,<sup>4, 13</sup> and Villiers.<sup>5</sup> However, attempts to detect and characterise these complexes in solution and to evaluate their relevance to possible catalytic processes using <sup>13</sup>C NMR have been unsuccessful.<sup>7d</sup> While equilibrium constants of some amine-CO<sub>2</sub> complexations in pentane have been measured by Johnston et. al.,<sup>14</sup> no such data, even qualitative, is currently available with guanidines. In this communication, we report the first ATR-FTIR study of guanidine-CO<sub>2</sub> complexation in solution and its mechanistic implications in reactions between propargylamines and CO<sub>2</sub>.

Table 1 Basicity and nucleophilicity of amines/guanidines in this study

No.	Amine/ Guanidine	pK <sub>a</sub> (MeCN) <sup>[a]</sup>	pK <sub>a</sub> (THF) <sup>[a]</sup>	N (nucleophilicity in MeCN)
1	TBD	26.0 <sup>10</sup>	21.0 <sup>15</sup>	16.2 <sup>[b],16</sup>
2	MTBD	25.4 <sup>10</sup>	17.9 <sup>15</sup>	14.4 <sup>[b],16</sup>
3	DBU	23.9 <sup>10</sup>	16.8 <sup>15</sup>	15.3 <sup>17</sup>
4	TMG	23.3 <sup>10</sup>	15.3 <sup>15a</sup>	13.6 <sup>[b],16</sup>
5	TEA	18.5 <sup>18</sup>	12.5 <sup>19</sup>	17.1 <sup>20</sup>
6	DABCO	18.3 <sup>21</sup>		18.8 <sup>22</sup>

[a] pK<sub>a</sub> of the conjugated acid; [b] Data measured in dichloromethane.



**Fig. 1** Time evolution of ATR-FTIR spectra of reaction between CO<sub>2</sub> and THF solution of (a) TBD (7 mM); (b) MTBD (21 mM), followed by addition of water (2 x 6.6 eq.) and (c) TMG (8 mM), TEA (7 mM) or DABCO (9 mM). Data was collected every 30 seconds, at 8 cm<sup>-1</sup> resolution.

### 'Activation' of CO<sub>2</sub> with guanidines and amines

ATR-FTIR has been proven as an useful tool in monitoring chemical and physical processes involving CO<sub>2</sub>.<sup>23</sup> In the context of monitoring amine/guanidine and CO<sub>2</sub> complexation in solution, it is the ideal technique, exploiting the C=O stretching frequencies of CO<sub>2</sub> (2300 cm<sup>-1</sup>) and of the zwitterionic complexes (1600-1700 cm<sup>-1</sup>).

Solutions of TBD, MTBD, TMG, DABCO and TEA (Table 1) in anhydrous THF were treated with CO<sub>2</sub> at 1 atm/25 °C and the reaction progress was monitored by measuring the IR spectra over time. These organic bases were chosen to include active catalysts (TBD, MTBD, TMG) for the reaction in Scheme 2,<sup>9b</sup> and strong nucleophiles which are weaker bases (DABCO, TEA). THF was chosen as solvent due to the poor solubility of the zwitterionic complexes in MeCN, the preferred solvent for catalytic reactions. In all cases, introduction of CO<sub>2</sub> to the system resulted in rapid saturation of CO<sub>2</sub> in solution (within 60 seconds), as observed by the growth of its finger-print frequencies at ~2300 cm<sup>-1</sup> (stretching) and 660 cm<sup>-1</sup> (bending).<sup>24</sup>

Formation of two new sets of peaks in the carbonyl region was observed with TBD in THF (Fig. 1a). These are assigned to TBD.CO<sub>2</sub> complex (1683 cm<sup>-1</sup> (C=O) and 1564 cm<sup>-1</sup> (C=N)) and [TBDH][HCO<sub>3</sub>] (1595 cm<sup>-1</sup> (C=O) and 1657 cm<sup>-1</sup> (C=N)). The presence of these two species is consistent with observations of Pérez González and Jessop by solid state NMR, given the non-strictly-anhydrous operational conditions of our ATR-FTIR equipment.<sup>7d, 25</sup> The assigned frequencies are also in agreement with solid data, i.e. 1712 and 1605 cm<sup>-1</sup> for TBD.CO<sub>2</sub> and 1660 and 1600 cm<sup>-1</sup> for [TBDH][HCO<sub>3</sub>].<sup>5</sup> The difference in vibrational frequencies of TBD.CO<sub>2</sub> in the solid state and in THF solution could be attributed to solvation effects, which are significant with zwitterionic structures.<sup>26</sup>

Treatment of MTBD with CO<sub>2</sub> in THF in a similar fashion also resulted in rapid formation of two broad peaks in the carbonyl region (Figure 1b). A small decrease in the intensity of these peaks was observed after 30 seconds, accompanied by formation of a white precipitate. These were attributed to the formation of a saturated solution of MTBD.CO<sub>2</sub>, albeit with a small amount of [MTBDH][HCO<sub>3</sub>] due to the presence of moisture as with TBD. Portion-wise addition of water to the solution led to complete hydrolysis of the complex MTBD.CO<sub>2</sub> to [MTBDH][HCO<sub>3</sub>]. Consequently the frequencies were assigned to MTBD.CO<sub>2</sub> (1648

cm<sup>-1</sup> (C=O) and 1602 cm<sup>-1</sup> (C=N)) and [MTBDH][HCO<sub>3</sub>] (1598 cm<sup>-1</sup> (C=O) and 1620 cm<sup>-1</sup>, 1603 cm<sup>-1</sup> (C=N)). Two stretching frequencies were observed for [MTBDH]<sup>+</sup> due to its lack of symmetry and the assignments were confirmed by comparing with a spectrum of [MTBDH]Cl. The different electronic properties of the guanidines are also reflected in the lower C=O stretching frequency in MTBD.CO<sub>2</sub> compared to that of TBD.CO<sub>2</sub>. Bubbling nitrogen through the solution led to the disappearance of the peaks in the carbonyl region. This is the first successful observation of the formation of MTBD.CO<sub>2</sub> complex in solution.

**Table 2** Vibrational frequencies of guanidine-CO<sub>2</sub> complexes

Guanidine	Frequency (cm <sup>-1</sup> )	Assignment
TBD	1683	C=O
	1564	C=N
MTBD	1648	C=O
	1602	C=N

Surprisingly, no new peak in the carbonyl region or precipitate was observed when solutions of TMG, TEA and DABCO were treated with CO<sub>2</sub> (Figure 1c). This indicates no detectable complexation between these amines and TMG with CO<sub>2</sub> in THF or acetonitrile. While a low value equilibrium constant ( $K = 0.046$ ) has been reported for TEA.CO<sub>2</sub>,<sup>14</sup> TMG is much more basic and DABCO is much more nucleophilic than TEA (Table 1). Thus, factors other than these are important in this type of complexes. These experimental results are consistently reproduced by our *ab initio* studies. Optimisation of the amine/guanidine-CO<sub>2</sub> complexes in MeCN using the MP2/6-311G(d,p) method was investigated. Only the structures of TBD.CO<sub>2</sub> and MTBD.CO<sub>2</sub> could be successfully optimised to a minimum without breaking the N-CO<sub>2</sub> bond ( $\leq 1.8$  Å). The optimised structures of TBD.CO<sub>2</sub> and MTBD.CO<sub>2</sub> also exhibit significant charge delocalisation on the guanidine, in agreement with computational work by Villiers,<sup>5</sup> which could explain their stability.

### Evaluation of catalytic activity

As TMG has been shown to catalyse the addition of CO<sub>2</sub> to propargyl amines,<sup>9</sup> the lack of a TMG.CO<sub>2</sub> complex raised questions about the relevance of these complexes to the catalytic activity of guanidines. Thus, we re-examined the effects of catalyst and solvent in the reaction between propargylamines and CO<sub>2</sub> as reported by Costa (Scheme 2, X = NBn).<sup>9b, 9c</sup> This

reaction was reported to work well with TBD, MTBD, TMG and DBU as catalysts at 100-110 °C, 10 bar CO<sub>2</sub> in acetonitrile, supercritical CO<sub>2</sub> or under neat conditions. Importantly, the reaction also works in water using a bulky guanidine as catalyst and sodium bicarbonate as the source of CO<sub>2</sub>. In this study, five solvents of widely different polarity and proton-donating capability (DMSO, MeCN, EtOH, THF and toluene) were examined. Lower pressure of CO<sub>2</sub> (5 bar) and temperature (50–75 °C) were deliberately chosen to lower the efficiency of the catalysts for better comparison.

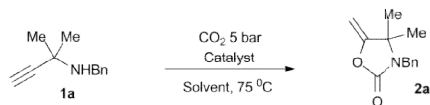
Preliminary experiments with the five solvents at 5 bar CO<sub>2</sub>, 50 °C gave little to no catalytic activity for DABCO and DMAP, or for reactions using THF and toluene as solvent, despite the strong complexation between CO<sub>2</sub> and MTBD/TBD in THF described above (supporting information, Table S1). The relevance of guanidine-CO<sub>2</sub> complexes in this type of catalytic reactions is consequently questioned. Subsequent reactions were performed at 75 °C and 5 bar of high purity CO<sub>2</sub>. The solvent and catalyst scopes were narrowed to MeCN/DMSO/EtOH and MTBD/TMG (Table 3). Despite its activity, DBU was not further considered in this study due to our focus on comparison to CO<sub>2</sub> complexation and poor chemical compatibility between DBU and our equipment.

While MTBD showed excellent catalytic activity in MeCN at 10 mol% as reported by Costa et. al.,<sup>9b</sup> only 8% conversion was observed at 1 mol% catalyst loading (Table 3, entries 1 and 5). TMG is a poorer catalyst in MeCN and EtOH (Table S1) but showed equal catalytic performance to MTBD/MeCN in DMSO (Table 3, entries 3 and 7). The lack of evidence for TMG.CO<sub>2</sub> complex in THF and the observed catalytic activity, albeit lower than in DMSO, in a protic solvent such as EtOH suggested that guanidine-CO<sub>2</sub> complexes may not be crucial for the reaction. As demonstrated with ATR-FTIR, addition of EtOH to a solution of MTBD.CO<sub>2</sub> and [MTBDH][HCO<sub>3</sub>] in THF led to complete disappearance of IR peaks belonging to MTBD.CO<sub>2</sub> (see supporting information).

The observed catalytic activity can be explained with a basicity-controlled mechanism. TMG is a weaker base than TBD and MTBD in acetonitrile. However, DMSO and EtOH are strongly polar solvents which can effectively stabilize TMGH<sup>+</sup>. The use of these solvents therefore enables TMG to be a more active catalyst. In order to verify this hypothesis on the origin of catalytic activity in these reactions, catalytic reactions using MTBD/MeCN, TMG/EtOH and TMG/DMSO combinations were performed again in the presence of a small amount of water (0.1 mL of H<sub>2</sub>O in 3.0 mL of organic solvent, Table 3, entries 2, 4, 6 and 8).

**Table 3** Conversion (%) of **1a** to **2a** using MTBD or TMG as catalyst<sup>[a,b]</sup>

No.	Catalyst	Loading (mol%)	Solvent		
			MeCN	EtOH	DMSO
1	MTBD	10	100	29	54
2 <sup>c</sup>	MTBD	10	99		



3	TMG	10	19	40	100
4 <sup>c</sup>	TMG	10		39	100
5	MTBD	1	8		
6 <sup>c</sup>	MTBD	1	8		
7	TMG	1		7	6
8 <sup>c</sup>	TMG	1		8	61

[a] Reaction were performed using 0.866 mmol of **1a** and catalyst in 3.0 mL of the specified solvent under 5 bar of CO<sub>2</sub> at 75 °C, 18h. [b]

55 Conversion was determined using <sup>1</sup>H NMR of the crude product.[c] Reaction performed in the presence of 0.1 mL H<sub>2</sub>O.

In all cases, no loss of catalytic activity was observed compared to the corresponding reaction under anhydrous conditions, further ruling out guanidine-CO<sub>2</sub> complexes as intermediates. Interestingly, the addition of water resulted in a 10 times increase in product yield using TMG/DMSO conditions at 1 mol% catalyst loading (Table 3, entry 8). This novel catalyst/solvent combination gave a far superior catalytic performance compared to the optimised MTBD/MeCN combination in the literature at 5 bar CO<sub>2</sub>, 75 °C.

## Conclusions

The first observation of cyclic guanidine-CO<sub>2</sub> complexes in solution by ATR-FTIR is reported, along with the lack of evidence for observable complexes with TMG and trisubstituted amines. Correlation between these observations and the catalytic activity of these nitrogen bases in reactions between propargylamines and CO<sub>2</sub> did not support activation of CO<sub>2</sub> via this mode of complexation. Instead, the basicity of the catalyst has been shown to be important to the catalytic activity. Consequently, polar solvents (e.g. DMSO), which can stabilize guanidinium cation, are beneficial to the reaction. Similar type of reactivity, i.e. via generation of strong nucleophile rather than direct activation of CO<sub>2</sub>, has also been proposed by Leitner and Hölscher in reaction of rhodium-alkyl complexes and CO<sub>2</sub>.<sup>27</sup> Finally, a novel catalyst/solvent combination (TMG/DMSO/H<sub>2</sub>O) with superior catalytic activity at low catalyst loading has been discovered. This may lead to much more sustainable process from propargylamines to cyclic carbamates using a commercially available and much less expensive catalyst.

## Acknowledgements

90 The authors thank Dr Andreas Kogelbauer (Imperial College London) and his group for access to a MultiMaxIR and Prof. Christopher Rayner (University of Leeds) for his insightful discussion. We thank the Royal Society for a research grant (RG100569). BNN thanks The Ramsay Memorial Trust and ICL 95 for his fellowship. SK thanks the Erasmus programme and the Friedrich-Alexander-Universität Erlangen-Nürnberg. RN thanks the University of Leeds for a University Research Scholarship.

## Notes and references

<sup>a</sup> Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK.

<sup>b</sup> Current address: School of Chemistry, University of Leeds, Leeds, West Yorkshire, LS2 9JT, UK. Tel: +44 (0)1133430109; E-mail: [b.nguyen@leeds.ac.uk](mailto:b.nguyen@leeds.ac.uk)

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1. (a) J. Schneider, H. Jia, J. T. Muckerman and E. Fujita, *Chem. Soc. Rev.*, 2012, **41**, 2036-2051; (b) A. Galia and G. Filardo, in *Carbon Dioxide as Chemical Feedstock*, ed. M. Aresta, Wiley-VCH, Weinheim, 2010, pp. 15-32.
2. (a) L. Dumeé, C. Scholes, G. Stevens and S. Kentish, *Int. J. Greenh. Gas. Con.*, 2012, **10**, 443-455; (b) G. T. Rochelle, *Science*, 2009, **325**, 1652-1654; (c) D. J. Heldebrant, C. R. Yonker, P. G. Jessop and L. Phan, *Energy Environ. Sci.*, 2008, 487-493.
3. (a) D. J. Heldebrant, P. K. Koech, M. T. C. Ang, C. Liang, J. E. Rainbolt, C. R. Yonker and P. G. Jessop, *Green Chem.*, 2010, **12**, 713; (b) P. G. Jessop, L. Phan, A. Carrier, S. Robinson, C. J. Dürr and J. R. Harjani, *Green Chem.*, 2010, **12**, 809-814.
4. E. R. Pérez, R. H. A. Santos, M. T. P. Gambardella, L. G. M. de Macedo, U. P. Rodrigues-Filho, J.-C. Launay and D. W. Franco, *J. Org. Chem.*, 2004, **69**, 8005-8011.
5. C. Villiers, J.-P. Dognon, R. Pollet, P. Thuéry and M. Ephritikhine, *Angew. Chemie. Int. Ed.*, 2010, **49**, 3465-3468.
6. C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine and T. Cantat, *Angew. Chemie. Int. Ed.*, 2012, **51**, 187-190.
7. (a) J. Ma, X. Zhang, N. Zhao, A. S. N. Al-Arifi, T. Aouak, Z. A. Al-Othman, F. Xiao, W. Wei and Y. Sun, *J. Mol. Catal. A: Chem.*, 2010, **315**, 76-81; (b) K. D. Vogiatzis, A. Mavrandonakis, W. Klopper and G. E. Froudakis, *ChemPhysChem*, 2009, **10**, 374-383; (c) X. Zhang, Y.-B. Jia, X.-B. Lu, B. Li, H. Wang and L.-C. Sun, *Tetrahedron Lett.*, 2008, **49**, 6589-6592; (d) F. S. Pereira, E. R. deAzevedo, E. F. da Silva, T. J. Bonagamba, D. L. da Silva Agostini, A. Magalhães, A. E. Job and E. R. Pérez González, *Tetrahedron*, 2008, **64**, 10097-10106; (e) B. Ochiai, K. Yokota, A. Fujii, D. Nagai and T. Endo, *Macromolecules*, 2008, **41**, 1229-1236; (f) X. Zhang, N. Zhao, W. Wei and Y. Sun, *Catal. Today*, 2006, **115**, 102-106; (g) A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Lett.*, 2003, **44**, 2931-2934; (h) J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller and J. S. Fowler, *Angew. Chemie. Int. Ed.*, 2009, **48**, 3482-3485.
8. (a) J. Meléndez, M. North, P. Villuendas and C. Young, *Dalton Trans.*, 2011, **40**, 3885-3902; (b) W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem. -Eur. J.*, 2010, **16**, 6828-6843.
9. (a) N. D. Ca, B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta and M. Costa, *Adv. Synth. Cat.*, 2011, **353**, 133-146; (b) M. Costa, G. P. Chiusoli, D. Taffurelli and G. Dalmonago, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1541-1546; (c) M. Costa, G. P. Chiusoli and M. Rizzardi, *Chem. Commun.*, 1996, 1699.
10. J. E. Taylor, S. D. Bull and J. M. J. Williams, *Chem. Soc. Rev.*, 2012, **41**, 2109.
11. (a) Y. H. Jhon, J.-G. Shim, J.-H. Kim, J. H. Lee, K.-R. Jang and J. Kim, *J. Phys. Chem. A*, 2010, **114**, 12907-12913; (b) K. R. Jorgensen, T. R. Cundari and A. K. Wilson, *J. Phys. Chem. A*, 2012, **116**, 10403-10411.
12. F. Joó, in *Physical Inorganic Chemistry: Reactions, Processes, and Applications*, ed. A. Bakac, Wiley, Hoboken, New Jersey, 2010, p. 247.
13. E. R. Pérez, M. O. da Silva, V. C. Costa, U. P. Rodrigues-Filho and D. W. Franco, *Tetrahedron Lett.*, 2002, **43**, 4091-4093.
14. J. C. Meredith, K. P. Johnston, J. M. Seminario, S. G. Kazarian and C. A. Eckert, *J. Phys. Chem.*, 1996, **100**, 10837-10848.
15. (a) T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito and I. A. Koppel, *J. Org. Chem.*, 2002, **67**, 1873-1881; (b) I. Kaljurand, T. Rodima, A. Pihl, V. Mäemets, I. Leito, I. A. Koppel and M. Mishima, *J. Org. Chem.*, 2003, **68**, 9988-9993.
16. B. Maji, D. S. Stephenson and H. Mayr, *Chemcatchem*, 2012, **4**, 993-999.
17. M. Baidya and H. Mayr, *Chem. Commun.*, 2008, 1792-1794.
18. J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, 1965, **87**, 5005-5010.
19. K. Abdur-Rashid, T. P. Fong, B. Greaves, D. G. Gusev, J. G. Hinman, S. E. Landau, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2000, **122**, 9155-9171.
20. J. Ammer, M. Baidya, S. Kobayashi and H. Mayr, *J. Phys. Org. Chem.*, 2010, **23**, 1029-1035.
21. Sigma-Aldrich, in *ChemFiles*, 2003, vol. 3, No. 1.
22. M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle and H. Mayr, *Angew. Chemie. Int. Ed.*, 2007, **46**, 6176-6179.
23. (a) L. Ohlin and M. Grahn, *J. Phys. Chem. C*, 2014, **118**, 6207-6213; (b) S. Hardy, I. M. de Wispelaere, W. Leitner and M. A. Liauw, *Analyst*, 2013, **138**, 819-824; (c) A. Buchard, F. Jutz, M. R. Kember, A. J. P. White, H. S. Rzepa and C. K. Williams, *Macromolecules*, 2012, **45**, 6781-6795; (d) Y. Yuan and A. S. Teja, *J. Supercrit. Fluids*, 2011, **56**, 208-212.
24. C. J. Pouchert, *Aldrich® Library of FT-IR Spectra: Vapor Phase*, Aldrich Chemical Co., Milwaukee, WI, 1989.
25. D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert and C. L. Liotta, *J. Org. Chem.*, 2005, **70**, 5335-5338.
26. (a) M. N. Blom, I. Compagnon, N. C. Polfer, G. von Helden, G. Meijer, S. Suhai, B. Paizs and J. Oomens, *J. Phys. Chem. A*, 2007, **111**, 7309-7316; (b) J. H. Jensen and M. S. Gordon, *J. Am. Chem. Soc.*, 1995, **117**, 8159-8170.
27. A. Uhe, M. Hölscher and W. Leitner, *Chem. -Eur. J.*, 2012, **18**, 170-177.