Exceptionally Active Catalysts for the Formation of Carbamates from Alcohols and Isocyanates: Molybdenum(VI) Dichloride Dioxide and Its DMF Complex

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Abstract: Small amounts of MoO_2Cl_2 or $MoO_2Cl_2(DMF)_2$ catalyze carbamate formation from an alcohol and isocyanates: 0.1 mol% of the respective additive allow primary, secondary or tertiary alcohols to add to aliphatic or aromatic isocyanates of varied steric hindrance within 20 minutes at room temperature. Typically the corresponding carbamate resulted in 100% yield. Only particularly hindered substrates required 1.0 mol% of the catalyst while as little as 0.01% sufficed for the phenylcarbamoylation of menthol. Catalytic amounts of DMAP accelerate carbamate formation from certain alcohols and isocyanates, too.

Key words: addition, carbamoylation, DMAP, heterocumulene, urethane formation

Carbamates are of pivotal importance because of their occurrence in polyurethanes and polyurethane foams.[1] Scattered usage of carbamates is made in insecticides[2] or pharmaceuticals.[3] In the laboratory, carbamates are intermediates of the Curtius degradation route to amines. They abound as nitrogen or oxygen protecting groups, directing agents for aromatic[4] or aliphatic lithiations,[5] and in asymmetric synthesis as a constituent of oxazolidinone auxiliaries.[6]

Arguably, the most frequently employed synthesis of carbamates is the addition of alcohols to isocyanates.[7] In principle this addition works fine as such. For non-hindered alcohols and aromatic isocyanates it is so reliable that in qualitative functional group analysis it was recognized as a proof for the presence of such an alcohol. Sterically hindered alcohols and/or isocyanates are known to provide carbamates upon sheer heating,[8] possibly in the respective alcohol as the solvent, or by accelerating their reaction by an additive. Depending on whether the latter is used in stoichiometric or overstoichiometric amounts or whether substoichiometric amounts suffice, such additives may be classified as 'promotors' or genuine 'catalysts'. Promotors of carbamate formation from alcohols and isocyanates are lithium[9] or potassium[10] alkoxides, DBU,[11] DMAP (Scheme 1[12–14]), Me_3SiCl,[15] CuCl,[16,13] CuCl–Bu_4NCl,[17] and CuBr·SMe_2.[18] Catalysts for carbamate formation from alcohols and isocyanates are lithium,[19] MeLi,[19] lithium alkoxide,[20] K_2CO_3/H_2O/EtOH,[21] Ti(O*i*-Pr)$_4$,[22] concentrated HCl,[23] Me_3SiCl,[24] tin carboxylates[25] [e.g. dibutyltin(IV) dilaurate[25a] or Sn(II) di(2-ethylhexanoate)[25b]], $SnCl_2·H_2O$,[26] SmI_2 in the presence of HMPA,[27] $SnCl_4$,[28] and unspecified amounts of $CuCl_2$.[29] For measure, Table 1 compiles such methods for the particularly demanding case of *tert*-alkylcarbamoylations of tertiary alcohols.

In polyurethane syntheses catalysts beside the mentioned ones are encountered. This may in part reflect the need to co-catalyze the urea-forming addition of amine, which is the by-product of hydrolytic in situ CO_2 formation, to residual isocyanate.

During ongoing work in this laboratory we had to convert the alcohols **10** and (*E*,*E*)-**13** into the corresponding *N*-phenyl carbamates **12** (Table 2) and (*E*,*E*)-**15** (Table 3), respectively. The presence of CO_2Me groups in these substrates, the fact that these esters were α,β-unsaturated, i.e. Michael acceptors, and the tendency of the desired carbamates to decompose through heat- or base-induced β-eliminations (→ respective α,β,γ,δ-unsaturated ester) put some serious restraints on viable reaction conditions. To our delight DMAP catalyzes both *N*-phenyl carbamoylations efficiently, which might be a first-time observation relative to the literature precedence shown in Scheme 1. DMAP seemed to be a better catalyst for that purpose than Et_3N when the alcohol **10** was concerned (Table 2). DMAP was definitely a superior catalyst compared to Et_3N for the carbamoylation of alcohol (*E*,*E*)-**13** (Table 3): in spite of employing only half as much DMAP (5 mol%) vs. Et_3N (10 mol%), of diluting the reactants threefold when DMAP rather than Et_3N was present, and of working at room temperature with DMAP but at 40 °C with Et_3N, the former reaction furnished almost as much carbamate (*E*,*E*)-**15** after 2.7 hours (83%) as resulted from the latter reaction after 6.5 hours (87%).

We noticed a certain sensitivity of carbamate (*E*,*E*)-**15** towards the excess of 0.1 equivalent of phenyl isocyanate (**14**), which we used. This implied the necessity of a chromatographic separation at high conversions. In order to circumvent this complication we started to search for an even better catalyst. We considered a number of literature conditions (cf. Table 1) less promising for our polyfunctional substrate. Accordingly, we tried additives of our own choice and included MoO_2Cl_2 because of the increasing number of transformations brought about by this catalyst[30–41a,42,43b,44] or its congeners $MoO_2Cl_2(DMF)_2$,[41b,43a,45,46] $MoO_2Cl_2(DMSO)_2$,[47–49] $MoO_2Cl_2(H_2O)_2$,[41a,43b] other spe-

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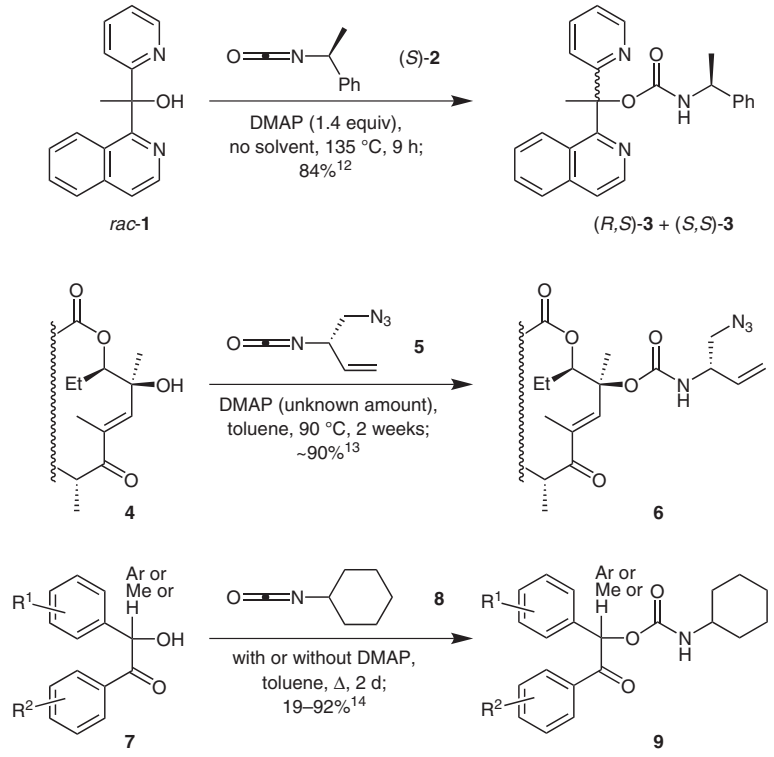


Scheme 1 DMAP-assisted carbamate syntheses from the literature

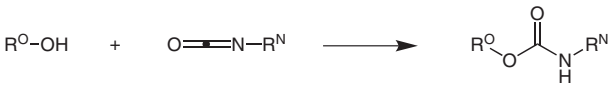
cies $MoO_2Cl_2L_2$[50] or MoO_2Cl_2(β-ketophosphonate).[51] Indeed, a suspension of MoO_2Cl_2 (5.0 mol%) in CH_2Cl_2 effected carbamate formation from alcohol (*E*,*E*)-**13** and phenyl isocyanate (**14**) at room temperature within barely over one hour. Carbamate (*E*,*E*)-**15** resulted in the hitherto highest yield (89%). Moreover, this specimen was easily purified because of the complete absence of the previously mentioned overreaction product.

Motivated by this success we optimized the novel carbamoylation towards another sterically hindered yet commercially available alcohol, namely towards (–)-menthol (**16**; Table 4). We lowered the MoO_2Cl_2 loading gradually from 5.0 mol% (entry 1) to 0.1% (entry 5) and always obtained an essentially quantitative yield of carbamate **17** after 20 minutes, aqueous workup, and purification by flash chromatography on silica gel.[52] We could even do without chromatography and still obtained a carbamate, which was pure according to its ^1H NMR spectrum (300 MHz) and the correctness (±0.30%) of its elemental analysis. For decreasing the catalyst loading even further we would have preferred working with a stock solution of the catalyst. This would have facilitated accurate dosages of the catalyst at preset values. However, MoO_2Cl_2 was completely insoluble in CH_2Cl_2 no matter how much solvent was employed. In an effort to escape this nuisance we synthesized $MoO_2Cl_2(DMF)_2$ from potassium molybdate, concentrated HCl, and DMF.[43a] We were surprised to find that $MoO_2Cl_2(DMF)_2$ was no more soluble in the concentration range of interest. It was nonetheless as good a catalyst as MoO_2Cl_2 for turning menthol (**16**) and phenyl isocyanate (**14**) into carbamate **17** at room temperature within 20 minutes (Table 4, entries 6 and 7). This included an experiment with just 100 ppm of $MoO_2Cl_2(DMF)_2$ (entry 7; quantitative yield). As far as we can tell both MoO_2Cl_2 and $MoO_2Cl_2(DMF)_2$ did not remain insoluble throughout the reaction but seemed to dissolve upon the addition of the isocyanate.

Since our $MoO_2Cl_2(DMF)_2$ was crystalline but MoO_2Cl_2 a fluffy powder, the former species was more conveniently weighed. For this reason all subsequent carbamoylations were performed exploiting $MoO_2Cl_2(DMF)_2$ rather than MoO_2Cl_2 catalysis. With the single exception of the sterically hindered carbamate depicted in Scheme 2, where we used 1.0 mol% $MoO_2Cl_2(DMF)_2$, we were satisfied to observe that as little as 0.1 mol% of the catalyst was enough to achieve uniform yields of ≥90%. In fact, most yields were quantitative.

Carbamate formations within 20 minutes at room temperature from a variety of alcohols and phenyl isocyanate (**14**) as the reference derivatizing agent are summarized in Table 5. Primary alcohols, benzyl alcohol, geraniol, and propargyl alcohol, as well as secondary alcohols, cyclohexanol and (–)-menthol, gave the respective carbamates **24**–**27** and **17** in 95% to quantitative yields. Tertiary alcohols, *tert*-butyl alcohol or 2-methyl-3-butyn-2-ol (**23**), did not react completely under the identical conditions yet they did so in the presence of 1.0 mol% rather than 0.1 mol% $MoO_2Cl_2(DMF)_2$: the respective carbamates **28** and **29** resulted in yields of 98% and more. However, alcohol **23** called for increased initial concentrations, perhaps due to inductively lowered nucleophilicity.

Table 1 Literature Syntheses of *N*,*O*-Di-*tert*-alkyl Carbamates from Tertiary Alcohols and Tertiary Isocyanates



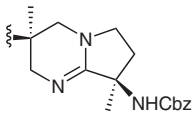
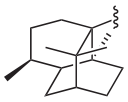
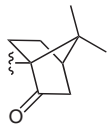
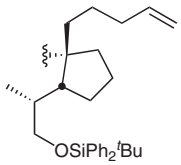
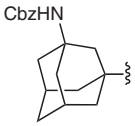
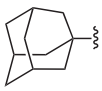
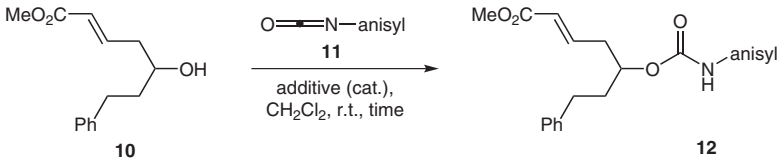
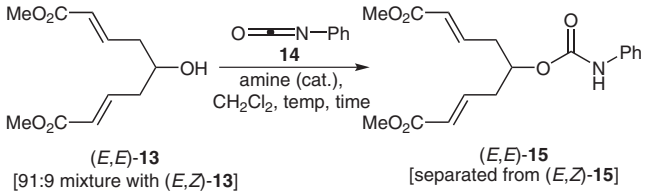
Entry	R^O	R^N	Additive	Temp	Time	Yield
1[8]			–	(jointly with Curtius rearrangement)		>45%
2[10]			*t*-BuOK (1.7 equiv)	0–23 °C	ca 1 h	>71%
3[9]			*n*-BuLi (1.0 equiv)	r.t.	uncertain	92%
4[22]			Ti(O*t*-Bu)$_4$ (10 mol%)	120 °C	96 h	56%
5[17]			CuCl, Bu_4NCl (2 + 2 equiv)	r.t.	–	38%
6[28]			$SnCl_4$ (6 mol%)	reflux; r.t.	1 + 17 h	>71%
7[15]			Me_3SiCl (1.4 equiv)	r.t.	5 h	78%
8[24]			Me_3SiCl (5 mol%)	r.t.	18 h	100%
9[23]			HCl (concd) (5 mol%)	r.t.	5 h	96%

Table 2 Carbamoylations of Alcohol **10** with Aryl Isocyanate **11**: DMAP Effect



Entry	Additive	mol% (amine)	$[\mathbf{10}]_0$	$[\mathbf{11}]_0$	Time	Yield
1	Et_3N	10	1.0 M	1.0 M	7 h	78%
2	DMAP	5	0.30 M	0.33 M	5 h	91%

Table 3 Carbamoylations of Alcohol (*E*,*E*)-**13** with *N*-Phenyl Isocyanate (**14**): DMAP and MoO_2Cl_2 Effects



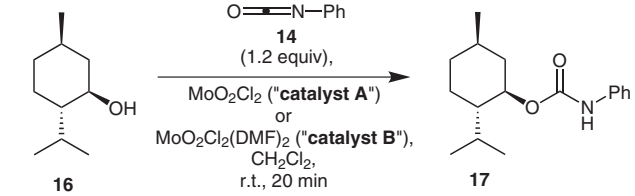
(*E*,*E*)-**13** [91:9 mixture with (*E*,*Z*)-**13**]

(*E*,*E*)-**15** [separated from (*E*,*Z*)-**15**]

Entry	Additive	mol% (amine)	$[\mathbf{13}]_0$	$[\mathbf{14}]_0$	Temp	Time	Yield
1	Et_3N	10	1.0 M	1.1 M	40 °C	6.5 h	87%
2	DMAP	5	0.30 M	0.33 M	r.t.	2.7 h	83%
3	MoO_2Cl_2	5	0.30 M	0.33 M	r.t.	70 min	89%

Swapping partners we also combined (–)-menthol (**16**) with a variety of isocyanates to yield the corresponding carbamates **34**–**39** and **17** (Table 6). Primary alkyl isocyanates (Bu, Bn) or aromatic isocyanates (with electronically varied *para*-substituents: Ac, H, OMe) provided ≥98% of their respective carbamate after 20 minutes. The sterically more hindered cyclohexyl isocyanate furnished carbamate **38** in slightly lower yield (90%). With the routine amount of 0.1 mol% $MoO_2Cl_2(DMF)_2$ *tert*-butyl isocyanate required 19 hours for converting (–)-menthol into carbamate **39** in 97% yield. A higher amount of the catalyst (1.0 mol%) lowered the time expenditure for attaining a quantitative yield to two hours.

Table 4 Carbamoylation of (–)-Menthol (**16**) with *N*-Phenyl Isocyanate (**14**) Catalyzed by Decreasing Amounts of MoO_2Cl_2 or $MoO_2Cl_2(DMF)_2$



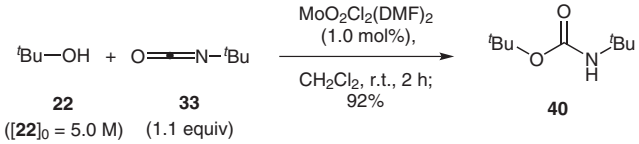
16 ($[\mathbf{16}]_0$ = 0.3 M)

17

Entry	Catalyst	mol% (catalyst)	Yield[a]
1	**A**	5	quant.
2	**A**	2	quant.
3	**A**	1	quant.
4	**A**	0.5	99%
5	**A**	0.1	98%[b]
6	**B**	0.1	quant.
7	**B**	0.01[c]	quant.

[a] All reactions provided analytically pure carbamate **17** after aqueous workup and removal of the solvent.
[b] After purification by flash chromatography.
[c] $[\mathbf{16}]_0$ = 1.0 M.

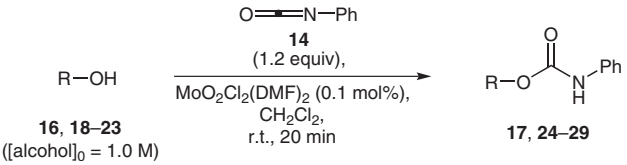
The most sterically hindered substrate combination, which we studied comprised of *tert*-butanol (**22**) and *tert*-butyl isocyanate (**33**; Scheme 2). In the presence of 1.0 mol% $MoO_2Cl_2(DMF)_2$ and after two hours we isolated 92% of the *N*,*O*-di-*tert*-butyl carbamate (**40**), provided we increased the alcohol concentration from 1.0 M to 5.0 M. Otherwise the yield of **40** reached 90% after nine hours.



22 ($[\mathbf{22}]_0$ = 5.0 M) **33** (1.1 equiv) **40**

Scheme 2 Carbamoylation of *tert*-butanol (**22**) with *tert*-butyl isocyanate (**33**) catalyzed by $MoO_2Cl_2(DMF)_2$

Table 5 Carbamoylation of Representative Alcohols with *N*-Phenyl Isocyanate (**14**) Catalyzed by $MoO_2Cl_2(DMF)_2$



16, **18**–**23** ($[\mathrm{alcohol}]_0$ = 1.0 M)

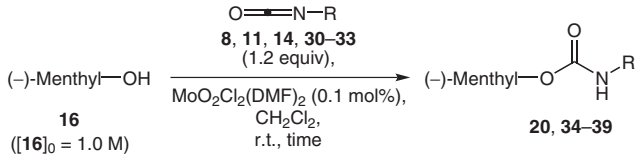
17, **24**–**29**

R	Alcohol	Carbamate	Yield[a]
Bn	**18**	**24**	quant.
geranyl	**19**	**25**	quant.
propargyl	**20**	**26**	quant.
cyclohexyl	**21**	**27**	95%
(–)-menthyl	**16**	**17**	quant.
t-Bu[b]	**22**	**28**	98%
α,α-dimethylpropargyl[c]	**23**	**29**	quant.

[a] All reactions provided analytically pure carbamate after aqueous workup and removal of the solvent.
[b] The reaction was carried out with 1.0 mol% of the catalyst.
[c] The reaction was carried out with 1.0 mol% of the catalyst and an initial alcohol concentration of 5.0 M.

In summary, we have developed an efficient method for the carbamoylation of alcohols with aliphatic and aromatic isocyanates.[54,55] In the presence of as little as 0.1 mol% of the inexpensive catalyst $MoO_2Cl_2(DMF)_2$ most car-

Table 6 Carbamoylation of (–)-Menthol (**16**) with Representative Isocyanates Catalyzed by $MoO_2Cl_2(DMF)_2$[53]



R	Isocyanate	Time (min)	Carbamate	Yield[a]
Bu	**30**	20	**34**	98%
Bn	**31**	20	**35**	quant.
4-acetylphenyl	**32**	20	**36**	quant.
Ph	**14**	20	**17**	quant.
4-methoxyphenyl	**11**	20	**37**	quant.
cyclohexyl	**8**	20	**38**	90%
t-Bu[b]	**33**	120	**39**	quant.

[a] All reactions provided analytically pure carbamate after aqueous workup and removal of the solvent.
[b] The reaction was carried out with 1.0 mol% of the catalyst.

bamoylation reactions proceeded to completion after 20 minutes at room temperature. Only tertiary substrates needed more time and/or higher catalyst loadings for reaching 90–100% yield like the less hindered substrates. The purity of our carbamates after aqueous workup but without chromatography was noteworthy. The mildness of our procedure suggests that it may be applied advantageously to many other polyfunctional substrates beside our Michael acceptors **10** and (*E*,*E*)-**13**.

References and Notes

(1) For polyurethane reviews, see: (a) Silva, A. L.; Bordado, J. C. *Catal. Rev.* **2004**, *46*, 31. (b) Moratti, S. C.; Charalambides, Y. C. *'Polymeric Carbamic Acids and Esters, and Their Sulfur Analogues', in 'Four Carbon–Heteroatom Bonds: X–C≡X, X=C=X, X_2C=X, CX_4', Science of Synthesis, Houben-Weyl Methods of Organic Chemistry*, Vol. 18; Knight, J. G., Ed.; Thieme: Stuttgart / New York, **2005**, 649–664.

(2) For example: *Propamocarb and Carbaryl: Römpp Online*, Version 3.1; Georg Thieme Verlag: Stuttgart, **2008**.

(3) (a) Rivastigmine: Winblad, B.; Grossberg, G.; Frölich, L.; Farlow, M.; Zechner, S.; Nagel, J.; Lane, R. *Neurology* **2007**, *69*, 14. (b) Retigabine: Blackburn-Munro, G.; Dalby-Brown, W.; Mirza, N. R.; Mikkelsen, J. D.; Blackburn-Munro, R. E. *CNS Drug Rev.* **2005**, *11*, 1. (c) Pardoprunox: Hauser, R. A.; Bronzova, J.; Sampaio, C.; Lang, A. E.; Rascol, O.; Theeuwes, A.; van de Witte, S. V. *Eur. Neurol.* **2009**, *62*, 40.

(4) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.

(5) (a) Hoppe, D.; Hense, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2282; *Angew. Chem.,* **1997**, *109*, 2376. (b) Beak, P.; Johnson, T. A.; Kim, D. D.; Lim, S. H.*Organolithiums in Enantioselective Synthesis* In *Top. Organomet. Chem.*, Vol. 5; Hodgson, D. M., Ed.; **2003**, 139–176.

(6) (a) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23. (b) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835. (c) Sibi, M. P. *Aldrichimica Acta* **1999**, *32*, 93.

(7) For carbamate reviews, see: (a) Rossi, L. in *'Four Carbon–Heteroatom Bonds: X–C≡X, X=C=X, X_2C=X, CX_4', Science of Synthesis, Houben-Weyl Methods of Organic Chemistry*, Vol. 18; Knight, J. G., Ed.; Thieme: Stuttgart / New York, **2005**, 461–648. (b) Chaturvedi, D.; Mishra, N.; Mishra, V. *Curr. Org. Synth.* **2007**, *4*, 308.

(8) Hutton, C. A.; Bartlett, P. A. *J. Org. Chem.* **2007**, *72*, 6865.

(9) Nikiforov, A.; Jirovetz, L.; Buchbauer, G. *Liebigs Ann. Chem.* **1989**, 489.

(10) Varie, D. L.; Beck, C.; Borders, S. K.; Brady, M. D.; Cronin, J. S.; Ditsworth, T. K.; Hay, D. A.; Hoard, D. W.; Hoying, R. C.; Linder, R. J.; Miller, R. D.; Moher, E. D.; Remacle, J. R.; Rieck, J. A. III.; Anderson, D. D.; Dodson, P. N.; Forst, M. B.; Pierson, D. A.; Turpin, J. A. *Org. Process Res. Dev.* **2007**, *11*, 546.

(11) Tsuji, T.; Nishida, S.; Okuyama, M.; Osawa, E. *J. Am. Chem. Soc.* **1995**, *117*, 9804.

(12) Elman, B.; Moberg, C. *Tetrahedron* **1986**, *42*, 223.

(13) Keyes, R. F.; Carter, J. J.; Zhang, X.; Ma, Z. *Org. Lett.* **2005**, *7*, 847.

(14) Cameron, J. F.; Willson, C. G.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2429.

(15) Andrade, R. B.; Martin, S. F. *Org. Lett.* **2005**, *7*, 5733.

(16) Duggan, M. I.; Imagire, J. S. *Synthesis* **1989**, 131.

(17) Nishikawa, T.; Urabe, D.; Tomita, M.; Tsujimoto, T.; Iwabuchi, T.; Isobe, M. *Org. Lett.* **2006**, *8*, 3263.

(18) Paleo, M. R.; Calaza, M. I.; Sardina, F. J. *J. Org. Chem.* **1997**, *62*, 6862.

(19) Cameron, J. F.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919.

(20) Cate, A. T.; Dankers, P. Y. W.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 6860.

(21) Dillard, R. D.; Poore, G. A.; Easton, N. R.; Sweeney, M. J.; Gibson, W. R. *J. Med. Chem.* **1968**, *11*, 1155.

(22) Spino, C.; Joly, M.-A.; Godbout, C.; Arbour, M. *J. Org. Chem.* **2005**, *70*, 6118.

(23) Benalil, A.; Roby, P.; Carboni, B.; Vaultier, M. *Synthesis* **1991**, 787.

(24) Villhauer, E. B.; Brinkman, J. A.; Naderi, G. B.; Burkey, B. F.; Dunning, B. E.; Prasad, K.; Mangold, B. L.; Russell, M. E.; Hughes, T. E. *J. Med. Chem.* **2003**, *46*, 2774.

(25) (a) Britain, J. W.; Gemeinhardt, P. G. *J. Appl. Polym. Sci.* **1960**, *4*, 207. (b) Francis, T.; Thorne, M. P. *Can. J. Chem.* **1976**, *54*, 24.

(26) White, D. K.; Greene, F. D. *J. Org. Chem.* **1978**, *43*, 4530.

(27) Kim, Y. H.; Park, H. S. *Synlett* **1998**, 261.

(28) Hodgson, D. M.; Thompson, A. J.; Wadman, S.; Keats, C. J. *Tetrahedron* **1999**, *55*, 10815.

(29) Finke, P. E.; Oates, B.; Mills, S. G.; MacCoss, M.; Malkowitz, L.; Springer, M. S.; Gould, S. L.; DeMartino, J. A.; Carella, A.; Carver, G.; Holmes, K.; Danzeisen, R.; Hazuda, D.; Kessler, J.; Lineberger, J.; Miller, M.; Schleif, W. A.; Emini, E. A. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2475.

(30) Review: Jeyakumar, K.; Chand, D. K. *J. Chem. Sci.* **2009**, *121*, 111.

(31) Jeyakumar, K.; Chand, D. K. *Synthesis* **2009**, 306.

(32) Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, 807.

(33) Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, 1685.

(34) Weng, S.-S.; Lin, Y.-D.; Chen, C.-T. *Org. Lett.* **2006**, *8*, 5633.

(35) Goswami, S.; Maity, A. C. *Tetrahedron Lett.* **2008**, *49*, 3092.

(36) Chen, C.-T.; Kuo, J.-H.; Pawar, V. D.; Munot, Y. S.; Weng, S.-S.; Ku, C.-H.; Liu, C.-Y. *J. Org. Chem.* **2005**, *70*, 1188.

(37) (a) Fernandes, A. C.; Fernandes, R.; Romão, C. C.; Royo, B. *Chem. Commun.* **2005**, 213. (b) Reis, P. M.; Romão, C. C.; Royo, B. *Dalton Trans.* **2006**, 1842.
(38) Fernandes, A. C.; Romão, C. C. *Tetrahedron Lett.* **2005**, *46*, 8881.
(39) Fernandes, A. C.; Romão, C. C. *J. Mol. Catal. A: Chem.* **2006**, *253*, 96.
(40) Fernandes, A. C.; Romão, C. C. *J. Mol. Catal. A: Chem.* **2007**, *272*, 60.
(41) (a) Fernandes, A. C.; Romão, C. C. *Tetrahedron* **2006**, *62*, 9650. (b) Sanz, R.; Escibano, J.; Fernández, Y.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synlett* **2005**, 1389.
(42) Cf. ref. 41a.
(43) (a) Sanz, R.; Escibano, J.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synthesis* **2004**, 1629. (b) Fernandes, A. C.; Romão, C. C. *Tetrahedron Lett.* **2007**, *48*, 9176.
(44) Jeyakumar, K.; Chand, D. K. *Tetrahedron Lett.* **2006**, *47*, 4573.
(45) Sanz, R.; Escibano, J.; Pedrosa, M. R.; Aguado, R.; Arnáiz, F. J. *Adv. Synth. Catal.* **2007**, *349*, 713.
(46) Note added in proof: During revision of our manuscript $MoO_2Cl_2(DMF)_2$ catalysis in reductive cyclizations of (*ortho*-nitroaryl)alkenes was reported by: Malakar, C. C.; Merisor, E.; Conrad, J.; Beifuss, U. *Synlett* **2010**, 1766.
(47) Sanz, R.; Aguado, R.; Pedrosa, M. R.; Arnáiz, F. J. *Synthesis* **2002**, 856.
(48) Arnáiz, F. J.; Aguado, R.; Martinez de Ilarduya, J. M. *Polyhedron* **1994**, *13*, 3257.
(49) Jeyakumar, K.; Chand, D. K. *Appl. Organomet. Chem.* **2006**, *20*, 840.
(50) (a) Bruno, S. M.; Balula, S. S.; Valente, A. A.; Almeida Paz, F. A.; Pillinger, M.; Sousa, C.; Klinowski, J.; Freire, C.; Ribeiro-Claro, P.; Gonçalves, I. S. *J. Mol. Catal. A: Chem.* **2007**, *270*, 185. (b) Bruno, S. M.; Pereira, C. C. L.; Balula, M. S.; Nolasco, M.; Valente, A. A.; Hazell, A.; Pillinger, M.; Ribeiro-Claro, P.; Gonçalves, I. S. *J. Mol. Catal. A: Chem.* **2007**, *261*, 79. (c) Bruno, S. M.; Fernandes, J. A.; Martins, L. S.; Gonçalves, I. S.; Pillinger, M.; Ribeiro-Claro, P.; Rocha, J.; Valente, A. A. *Catal. Today* **2006**, *114*, 263.
(51) Salles, L.; Nixon, A. F.; Russell, N. C.; Clarke, R.; Pogorzelec, P.; Cole-Hamilton, D. J. *Tetrahedron: Asymmetry* **1999**, 1471.
(52) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(53) **Typical Procedure for the Carbamoylation of Alcohols with Isocyanates**: At 22 °C neat benzyl isocyanate (**31**; 0.52 mL, 0.56 g, 1.1 equiv) was added to $MoO_2Cl_2(DMF)_2$ (1.3 mg, 3.8 μmol, 0.1 mol%) and 1.0 M (–)-menthol (**16**; 594 mg, 3.80 mmol) in CH_2Cl_2 (3.8 mL). The mixture was stirred at r.t. for 20 min. CH_2Cl_2 (10 mL) and H_2O (7 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (2 × 12 mL). The combined organic phases were dried over Na_2SO_4. Removal of the solvent under reduced pressure gave *N*-benzyl-*O*-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl] carbamate (**35**; 1.10 g, 100%) as a white solid (mp 92 °C). It was a pure compound as evidenced by ^{1}H NMR spectroscopy and combustion analysis.
(54) (a) Carbamates **12**, **15**, **36**, and **37** are new compounds.[55] Other carbamates were described (inter alia) in the following references: (b) Carbamates **17** and **34**: Gautschi, M. WO Patent, 2004/000023A1, **2003**. (c) Carbamate **24**: Leogane, O.; Lebel, H. *Synthesis* **2009**, 1935. (d) Carbamate **25**: Seemayer, R.; Liang, J. WO Patent, 2004/037827A1, **2004**. (e) Carbamates **26** and **29**: Newton, R.; Savage, G. P. *Aust. J. Chem.* **2008**, *61*, 432. (f) Carbamate **27**: Wiberg, K. B.; Wang, Y.-G.; Miller, S. J.; Puchlopek, A. L. A. *J. Org. Chem.* **2009**, *74*, 3659. (g) Carbamate **28**: Steinke, T.; Shaw, B. K.; Jong, H.; Patrick, B. O.; Fryzuk, M. D. *Organometallics* **2009**, *28*, 2830. (h) Carbamate **35**: Martínez, R.; Ramón, D. J.; Yus, M. *Adv. Synth. Catal.* **2008**, *350*, 1235. (i) Carbamate **38**: Kroetz, D. L.; Zeldin, D. C.; Hammock, B. D.; Morisseau, C. US Patent, 6531506B1, **2003**. (j) Carbamate **39**: Boghani, N.; Gebreselassie, P. WO Patent, 2006/127738A2, **2006**. (k) Carbamate **40**: Heydari, A.; Khaksar, S.; Tajbakhsh, M. *Synthesis* **2008**, 3126.
(55) All new compounds (**12**, **15**, **36,** and **37**) gave satisfactory ^{1}H NMR and ^{13}C NMR spectra and correct combustion analyses for C, H, and N (±0.30%). Analytical details will be published in a full paper in due course.