



[View PDF Version](#)

DOI: [10.1039/A802123F](https://doi.org/10.1039/A802123F) (Paper) Reference Section for: *J. Chem. Soc., Perkin Trans. 1*, 1998, 2047-2054

Synthesis and structures of 1,3,1',3'-tetrabenzyl-2,2'-biimidazolidinylidenes (electron-rich alkenes), their amination intermediates and their degradation products

(Note: The full text of this document is currently only available in the [PDF Version](#))

Bekir Çetinkaya, Engin Çetinkaya, José A. Chamizo, Peter B. Hitchcock, Hatam A. Jasim, Hasan Küçükbay and Michael F. Lappert

Abstract

Benzyl (R) substituted enetetramines 9 and 3 have been studied. From $\text{HNR}(\text{CH}_2)_2\text{NRH}$ and $\text{CH}(\text{NMe}_2)_2\text{O}^t\text{Bu}$ or $\text{CH}(\text{OMe})_2\text{NMe}_2$, two new intermediates along the pathway to 9, namely the orthoamide 11 and the bis(orthoamide) 12 were isolated. Each of 11 and 12 was converted into 9 by refluxing in toluene. Photolysis of 9 yielded the isomer 10, while thermolysis of 9 gave the di(debenzylated) product 1,1'-dibenzyl-2,2'-biimidazoline 13. A route to 3 ($\text{R} = \text{R}' = \text{CH}_2\text{Ph}$) similar to those used for 9, involving the condensation of 1,2- $\text{C}_6\text{H}_4[\text{N}(\text{R})\text{H}]_2$ with $\text{CH}(\text{OMe})_2\text{NMe}_2$, or the reaction between 1,3-dibenzylbenzimidazolium chloride 8 ($\text{X} = \text{Cl}$) and NaH, did not give the expected enetetramine 3 (the dibenzo-analogue of 9), the bis(debenzylated) product 15 being obtained instead. Heating the orthoamide 1,2- $\text{R}'\text{NC}_6\text{H}_4\text{N}(\text{R})\text{C}(\text{H})\text{NMe}_2$, prepared from $\text{CH}(\text{NMe}_2)_2\text{O}^t\text{Bu}$ and 1,2- $\text{C}_6\text{H}_4[\text{N}(\text{H})\text{R}]_2$, also gave 15. The reactions of S_8 , PhNCS or KOH with a mixture of 8 ($\text{X} = \text{Cl}$) and NaH gave 17, 18 or 19, respectively, consistent with the transient formation in each reaction of the tetrabenzylenetetramine 3 ($\text{R} = \text{R}' = \text{CH}_2\text{Ph}$). The molecular structure of each of the crystalline compounds 10, 11, 12 and 13 was established by X-ray diffraction.

References

1. B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, D. B. Shaw, K. Spyropoulos and N. J. W. Warhurst, *J. Organomet. Chem.*, 1993, **459**, 311 [CrossRef](#) [CAS](#).
2. M. F. Lappert, *J. Organomet. Chem.*, 1988, **358**, 185 [CrossRef](#).
3. E. Çetinkaya, P. B. Hitchcock, H. Küçükbay, M. F. Lappert and S. Al-Juaid, *J. Organomet. Chem.*, 1994, **481**, 89 [CrossRef](#) [CAS](#).
4. H. Goldwhite, J. Kaminski, G. Millhauser, J. Ortiz, M. Vargas, L. Vertal, M. F. Lappert and S. J. Smith, *J. Organomet. Chem.*, 1986, **310**, 21 [CrossRef](#) [CAS](#).
5. B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert and J. B. Pedley, *J. Chem. Soc., Chem. Commun.*, 1971, 1370 [RSC](#).
6. M. F. Lappert and R. K. Maskell, *J. Chem. Soc., Chem. Commun.*, 1982, 580 [RSC](#).
7. R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1968, **11**, 754 [CrossRef](#) [CAS](#); J. Hocker and R. Merten, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 964 [CAS](#); F. Roeterdink, J. W. Scheeren and W. H. Laarhoven, *Tetrahedron Lett.*, 1983, **24**, 2307 [CrossRef](#) [CAS](#).
8. D. J. Cardin, M. J. Doyle and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1972, 927 [RSC](#).
9. (a) A. J. Arduengo, J. R. Goerlich and W. F. Marshall, *Liebigs Ann. Recl.*, 1997, 365 [Search PubMed](#) and refs. cited therein; (b) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2163.
10. H. E. Winberg, J. E. Carnahan, D. D. Coffman and M. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 2055 [CrossRef](#) [CAS](#).
11. P. B. Hitchcock, M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2160 [RSC](#).
12. E. Çetinkaya, P. B. Hitchcock, H. A. Jasim, M. F. Lappert and K. Spyropoulos, *J. Chem. Soc., Perkin Trans. 1*, 1992, 561 [RSC](#).
13. A. W. Coleman, P. B. Hitchcock, M. F. Lappert, R. K. Maskell and J. H. Müller, *J. Organomet. Chem.*, 1985, **296**, 173 [CrossRef](#) [CAS](#).
14. P. B. Hitchcock, M. F. Lappert, P. Terreros and K. P. Wainwright, *J. Chem. Soc., Chem. Commun.*, 1980, 1180 [RSC](#).
15. J. A. Chamizo and M. F. Lappert, *J. Org. Chem.*, 1989, **54**, 4684 [CrossRef](#) [CAS](#).
16. J. A. Chamizo, P. B. Hitchcock, H. A. Jasim and M. F. Lappert, *J. Organomet. Chem.*, 1993, **451**, 89 [CrossRef](#) [CAS](#).
17. (a) H.-W. Wanzlick, F. Esser and H.-J. Kleiner, *Chem. Ber.*, 1963, **96**, 1208 [CrossRef](#) [CAS](#); (b) H.-W. Wanzlick and E. Schikora, *Angew. Chem.*, 1960, **72**, 494 [CrossRef](#) [CAS](#).

18. (a) R. W. Alder and M. E. Blake, *Chem. Commun.*, 1997, 1513 [RSC](#); (b) M. Wenzel, D. Lindauer, R. Beckert, R. Boese and E. Anders, *Chem. Ber.*, 1996, **129**, 39 [CrossRef](#) [CAS](#); (c) M. K. Denk, A. Thadani, K. Hatano and A. J. Lough, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2607 [CrossRef](#) [CAS](#).
19. J. Daub, A. Hasenhündl, K. P. Krenkler and J. Schmetzer, *Liebigs Ann. Chem.*, 1980, 997 [Search PubMed](#).
20. J. E. Baldwin, S. E. Branz and J. A. Walker, *J. Org. Chem.*, 1977, **42**, 4142 [CrossRef](#) [CAS](#); J. E. Baldwin and J. A. Walker, *J. Am. Chem. Soc.*, 1974, **96**, 596 [CrossRef](#) [CAS](#).
21. K. Spyropoulos, D. Phil. Thesis, University of Sussex, 1985.
22. K. H. Taffs, L. V. Prosser, F. B. Wigton and M. M. Joullié, *J. Org. Chem.*, 1961, **26**, 462 [CrossRef](#) [CAS](#).
23. S. Miyano, M. Nawa, A. Mori and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2171 [CAS](#).
24. C. K. Fair, MOLEN—a Structure Determination System, Enraf-Nonius, Delft, 1990.
25. P. Main, G. Germain and M. Woolfson, MULTAN—a Program for Automatic Solution of Crystal Structures, University of York, 1984.