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Reduction of the Isolated Double Bond in Bis(*N*-Alkenylbenzimidazole)Pd(II) Complexes with KBH_4

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Abstract

Palladium(II)-promoted vicinal diamination of *N*-alkenylbenzimidazoles has been investigated. Dichlorobis(1-(alkenyl)benzimidazole)palladium(II) complexes were identified as initial reaction products which proved to be rather inert to the subsequent oxidative diamination required in the process. Instead, they were readily reduced by KBH_4 to give the corresponding 1-alkylbenzazoles as the main reaction products. The crystal structure of the isolated complex *trans*-dichlorobis(1-(3-butenyl)benzimidazole)palladium(II) was determined by X-ray diffraction analysis.

Keywords: *Palladium and compounds, alkenes, reduction, boron and compounds*

The chelating properties of ethylenediaminotetraacetic acid (EDTA) are well documented.[1] The presence of iminodiacetic acid units allows it to form stable complexes with almost all cations, giving chelate rings. These properties have been used in chemical analysis, biological applications, in the complexation of heavy metals in nuclear medicine[2] and as contrast agents in magnetic resonance imaging.[3] In spite of the high capability of heterocyclic rings as nitrogen-donor ligands,[4] very few complexones[1] have incorporated such rings in their structure. Only some pyridine and 2,2'-bipyridine derivatives have been described.[5] Our previous experience with azole-containing ligands[6] prompted us to prepare EDTA-like structures which contain an azole ring as an additional donor site to improve its metal complexation capabilities.

Although the synthesis of such molecules could be achieved by different approaches, we selected the direct *vic*-diamination of *N*-alkenylbenzimidazoles, compounds easily prepared by alkylation of benzimidazole with haloalkenes. There are several methods reported in the literature for metal catalyzed *vic*-diamination of olefins including Tl(III),[7] Hg(II),[8] and Os(IV).[9] We chose the palladium(II)-promoted vicinal diamination[10] of olefins described by Bäckvall in 1978.[11] This potentially useful stereospecific *cis* diamination has rarely been used and only simple alkenes are diaminated with dimethylamine by this procedure. This "one-pot" reaction implies the formation of intermediate aminopalladation product, followed by the *in situ* oxidation of Pd(II) which then undergoes a nucleophilic displacement by the amine. Final reduction with KBH_4 yields Pd(0) species which are easily removed from the reaction medium.

In our case, the reactions were performed with $HN(CH_2CO_2Me)_2$ as the amine partner and *N*-alkenylbenzimidazoles as the starting alkenes. The results were compared with that obtained with dimethylamine **2a** or di-*n*-butylamine **2c** as alternative amines. As indicated in Table 1, the aminopalladation of *N*-alkenylbenzimidazoles **1a,b** gave exclusively alkanes **3a,b** without traces of diamines **4a-d**.

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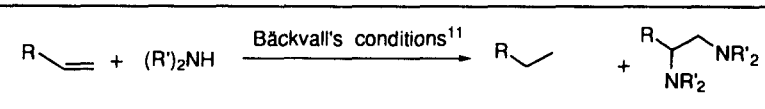
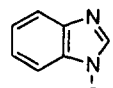
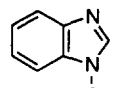
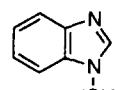
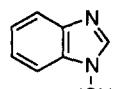
Table 1: Results obtained in the Aminopalladation of *N*-Alkenylbenzimidazoles **1a,b**



1a,b **2a-c** **3a,b** **4a-d**

R	R'	1a,b(%)	3a,b (%)	4a-d(%)
 **1a**	Me **2a**	**1a** (15)	**3a** (85)	**4a** (0)
	CH_2CO_2Me **2b**	**1a** (0)	**3a** (100)	**4b** (0)
 **1b**	CH_2CO_2Me	**1b** (11)	**3b** (89)	**4c** (0)
	*n*-Bu **2c**	**1b** (10)	**3b** (90)	**4d** (0)

Bäckvall's conditions: i: $[PdCl_2Ph(CN)_2]$/THF; ii: $(R')_2NH$; iii: MCPBA; iv: $NaBH_4$/KOH
Yields are given by GC considering the amount of overall conversion

These results contrast notably with those previously reported[11] in the *vic*-diamination of simple alkenes, in which high yields of diamines were obtained. Present results can be explained considering the influence of the benzimidazole ring in the reaction pathway. A benzonitrile ligand exchange[12] in bis(benzonitrile)palladium(II) chloride $[PdCl_2(PhCN)_2]$ by the benzimidazole ring takes place to give new complexes $[PdCl_2(AzolN\text{-})_2]$, which prevent the oxidative diamination. Instead, these complexes are able to activate reduction of the double bond by KBH_4, in the last step of the one pot reaction. In fact, treatment of 1-(3-butenyl)benzimidazole **1b** with $[PdCl_2(PhCN)_2]$ at 0 °C gave complex **5** as crystalline yellow needles which contained **1b** as a ligand.

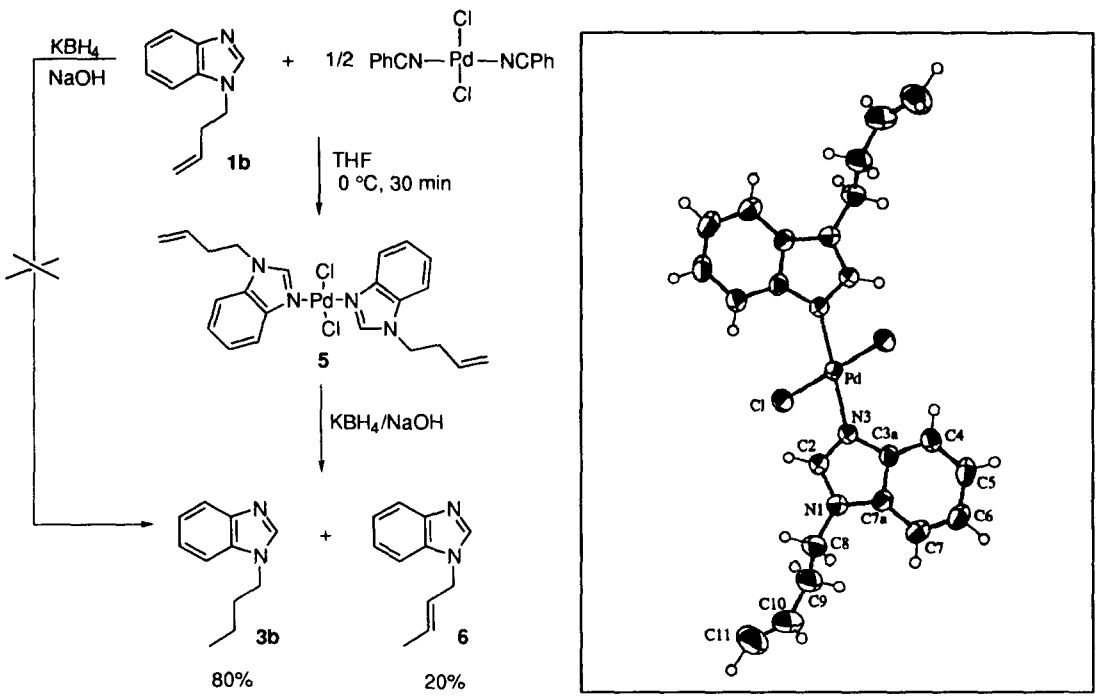
X-ray diffraction analysis of **5** revealed that the Pd atom is coordinated in a square-planar fashion to the Cl and N atoms. This coordination has previously been described for *trans*-dichlorobis(1-methylimidazole)-palladium(II).[13]

Reaction of complex **5** with KBH_4/NaOH in THF, the conditions used in the last step of the Bäckvall procedure, produces reduction and migration of the double bond to give 1-butylbenzimidazole **3b** and 1-crotylbenzimidazole **6** respectively. This reduction did not take place with the uncomplexed alkenes **1a** or **1b** (Scheme 1).

Reduction of isolated alkenes has been previously reported with $NaBH_4$ using Co(II) or Ni(II) salts as co-reagents.[14] To our knowledge, this is the first communication showing Pd(II) mediated reduction of unactivated double bounds with borohydride.

Furthermore, the present study shows that palladium mediated oxidative *vic*-diamination is prevented if a nitrogen containing heterocycle is present in the olefin.

Scheme 1



X-ray structure of Complex **5**

***trans*-Dichlorobis(1-(3-butenyl)benzimidazole)palladium(II) (5).** To a solution of 1-(3-butenyl)benzimidazole **1b** (100 mg, 0.58 mmol) in dry THF (3 mL) at 0 °C bis(benzonitrile)palladium(II) chloride (111 mg, 0.29 mmol) was added. The reaction mixture was stirred at 0 °C during 30 min. The precipitate was filtered off and the yellow solid was dried *in vacuo*. mp 203-205 °C (decomp) (from dry THF). ^{1}H NMR ($CDCl_3$) δ 2.65 (q, 2H, ^3J = 7.1 Hz), 4.25 (t, 2H, ^3J = 7.1 Hz), 5.13 (dd, 1H, $^3J_{trans}$ = 17.1 Hz, ^4J = 1.3 Hz), 5.17 (d, 1H, $^3J_{cis}$ = 10.3 Hz), 5.79 (ddt, 1H, $^3J_{trans}$= 17.1 Hz, $^3J_{cis}$ = 10.3 Hz, ^3J = 7.1 Hz), 7.37-7.38 (m, 2H, H7, H6), 7.43 (m, 1H, H5), 8.32 (s, 1H, H2), 8.55 (d, 1H, ^3J = 8.1 Hz, H4); ^{13}C NMR ($CDCl_3$) δ 33.6 (d, J = 129.1 Hz) 45.6 (t, J = 141.2 Hz), 110.1 (d, C7, J = 163.6 Hz), 119.2 (t, J = 156.9 Hz), 121.1 (d, C4, J = 167.7 Hz), 123.8 (d, C5, J = 165.2 Hz), 124.4 (d, C6, J = 162.3 Hz), 132.4 (s, C7a), 132.6 (d, J = 154.6 Hz), 140.3 (s, C3a), 143.8 (d, C2, J = 211.4 Hz); IR (nujol) n 3110, 1640, 1610, 1515, 1460, 1375. 1300, 1250, 1200 cm^{-1}. Anal. Calcd. for $C_{22}H_{24}N_4Cl_2Pd$: C, 50.64; H, 4.64; N, 10.74. Found: C, 50.79; H, 4.54; N, 10.72.

Reduction of complex 5 with KBH_4. Complex **5** (7.4 mg, 0.014 mmol), KBH_4 (0.8 mg, 0.014) and 50 ml of a 2M NaOH solution, were stirred in dry THF (1 mL) at room temperature for 15 min. The palladium black was filtered off and washed with ether. The ^{1}H NMR spectra of the crude, showed two products **3b** (80%) ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, ^3J = 7.4 Hz), 1.28 (m, 2H), 1.79 (m, 2H), 4.11 (t, 2H, ^3J = 7.1 Hz), 7.19-7.24 (m, 2H, H5, H6), 7.35 (dd, 1H, H7, ^3J = 6.8 Hz,^4J = 1.7 Hz), 7.66 (dd, 1H, H4, ^3J = 6.8 Hz, ^4J = 1.8 Hz), 7.84 (s, 1H, H2); ^{13}C NMR ($CDCl_3$) δ 13.4 (q, J = 125 Hz), 19.9 (t, J = 125 Hz), 31.7 (t, J = 128 Hz), 44.9 (t, J = 138 Hz), 109.6 (d, C7, J = 160 Hz), 120.4 (d, C4, J = 160 Hz), 122.0 (d, C5, J = 160 Hz), 122.8 (d, C6, J = 161 Hz), 124,8 (s, C7a), 142.9 (d, C2, J = 204 Hz), 143,8 (s, C3a); MS m/z 174 (39, M^+), 131 (100), and 1-crotylbenzimidazole **6** (20%) ^{1}H NMR ($CDCl_3$) δ 1.72 (d, 3H, ^3J = 7.6 Hz), 4.70 (dd, 2H, ^3J = 7.2 Hz, ^4J = 1.26 Hz), 5.62-5.68 (m, 1H), 5.72-5.82 (m, 1H), 7.20-7.31 (m, 2H), 7.32-7.38 (m, 1H), 7.76-7.82 (m, 1H), 7.89 (s, 1H); MS m/z 172 (39, M^+), 131 (100).

Crystal structure determination. Crystals of complex **5** were obtained from THF. The compound is monoclinic, space group $P2_1/n$. The Pd atoms lie on a crystallographic center of symmetry. Intensities were corrected for Lorentz and polarization effects; the structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located on a difference Fourier map and refined isotropically except for the H atoms attached to C-11 which were maintained fixed.

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References

(1) Anderegg, G. *Complexones* in *Comprehensive Coordination Chemistry:* Vol 2, ed. by G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon Press, New York, 1987, pp 777-792.

(2) Jones, C. J. *Applications in the Nuclear Fuel Cycle and Radiopharmacy* in *Comprehensive Coordination Chemistry* Vol 6, ed. by G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon Press, New York, 1987, p. 881-1009.

(3) (a) Andrew, E. R.; Byder, G.; Griffith, J.; Iles, R.; Styles, P. in *Clinical Magnetic Resonance Imaging and Spectroscopy*, John Wiley & Sons. New York, 1990. (b) Peters, J. A.; Huskens, J.; Raber, D. J. *Prog. N.M.R. Spectroscopy*, **1996**, *28*, 283 and references therein. (c) Berton, G. Ed. *Handbook of Metal-Ligand Interactions in Biological Fluids. Bioinorganic Chemistry*, Vol. 2, Marcel Dekker, New York, 1995.

(4) (a) Steel, P. J. *Coord. Chem. Rev.* **1990,** *106*, 227-265. (b) Sorrell, T. N. *Tetrahedron*, **1989,** *45*, 3-68.

(5) (a) Wagner, M.; Ruloff, R.; Hoyer, E.; Gründer, W. *Z.-Naturforsch-C*, **1997**, 52, 508-515. (b) Mukkala, V.-M.; Kankare, J. *Helv. Chim. Acta*, **1992**, *75*, 1578-1592. (c) Mukkala, M. Kwiatkowski, V.-M.; Kankare, J.; Takalo, H. *Helv. Chim. Acta*, **1993**, *76*, 893-899.

(6) (a) Ballesteros, P.; López, C.; López, C.; Claramunt, R. M.; Jimenez, J. A.; Cano, M.; Heras, J. V.; Pinilla, E.; Monge, A. *Organometallics*, **1994**, *13*, 289-297 (b) López Gallego-Preciado, M. C.; Ballesteros, P.; Claramunt, R. M.; Cano, M.; Heras, J. V.; Pinilla, E; Monge, A. *J. Organomet. Chem.* **1993**, *450*, 237-244. (c) López, M. C.; Claramunt, R. M.; Ballesteros, P. *Heterocycles*, **1994**, *37*, 891-896, and references cited therein.

(7) Aranda, V. G.; Barluenga, J.; Aznar, F. *Synthesis* **1974**, 504-505.

(8) Barluenga, J.; Alonso-Cires, N.; Asensio, G. *Synthesis*, **1979**, 962-964.

(9) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420-3426.

(10) Tsuji, J. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis.* John Wiley & Sons, N: Y. 1996.

(11) Bäckvall, J.-E. *Tetrahedron Lett.* **1978**, 163-166.

(12) (a) Cross, R. J. *Substitution Reactions of Inert-Metal Complexes-Coordination* Numbers 4 and 5, in Mechanisms of Inorganic and Organometallic Reactions, Twigg, M. V. Ed. Vol. 5, Plenum Press, New York, 1988, pp 117-137. (b) Adams, H.; Bailey, N. A.; Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Marcos, M.; Ridway, Ch.; Smith, A. J.; Styring, P.; Maitlis, P. M. *Liq. Crystals*, **1987**, *2*, 381-393.

(13) Navarro-Ranninger, M. C.; Martínez-Carrera, S.; Carcía-Blanco, S. *Acta Cryst.* **1983**, C39, 186-188.

(14) (a) Chung, S.-K. *J. Org. Chem.* **1979**, *44*, 1014-1016. (b) Wade, R. C. *J. Mol. Catal.* **1983**, *18*, 273-297. (c) Osby, J. O.; Heinzman, S. W.; Ganem, B. *J. Am. Chem. Soc.* **1986**, *108*, 67-72.