Porphodimethene–Zirconium: A New Entry into **Zirconium Macrocycle Organometallic Chemistry**

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Summary: The cis-dichloro-meso-hexaethylporphodimethene–zirconium(IV) complex has been functionalized to the corresponding dialkyl derivatives [R = Me, PhCH₂, Ph], **3–5**, displaying a variety of migratory pathways. In the case of benzyl derivative **4**, the spontaneous migration of the first benzyl to the ligand, **6**, is followed by the second one, photochemically induced, thus forming a Zr-porphyrinogen complex, **7**. The methyl derivative undergoes thermally induced methane elimination with the metalation of the meso ethyl chains, **8**. Migration of both methyl groups has been observed in the reaction of **3** with Bu^tNC, with the preliminary formation of η^2 -imine, rearranging to the corresponding enamine, **9**.

Macrocycles have had a remarkable development quite recently as ancillary ligands in the early transition metallorganic chemistry.¹ The metal *par excellence* chosen within the context has so far been zirconium in combination with tmtaa [tmtaa = dibenzotetramethyltetraaza[14]annulene],² calix[4]arenes,³ azatranes,⁴ porphyrinogens,⁵ and porphyrins.⁶ A quite recent synthetic methodology has made available the possibility of largescale production of the dianionic macrocycle *meso*-





hexaethylporphodimethene (see Scheme 1),⁷ which paves the way from porphyrinogen to porphyrin and combines some of the features of both skeletons.

This is a preliminary report on the organic chemistry of zirconium based on the porphodimethene ligand, with the purpose of emphasizing (i) the synthesis of Zr-C functionalities, (ii) the migration of an alkyl group from the metal either to the macrocyclic ligand or to an incoming substrate, and (iii) the intramolecular metalation of aliphatic C-H bonds.

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⁽¹⁾ For leading references on organometallic chemistry based on macrocyclic ligands see refs 2-6.

⁽²⁾ For tmtaa [dibenzotetramethyltetraaza[14]annulene], see: (a) Mountford, P. Chem. Soc. Rev. 1998, 27, 105, and references therein.
(b) Floriani, C.; Ciurli, S.; Chiesi-Villa, A.; Guastini, C. Angew. Chem., Int. Ed. Engl. 1987, 26, 70. (c) Solari, E.; De Angelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Inorg. Chem. 1992, 31, 96. (d) De Angelis, S.; Solari, E.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Inorg. Chem. 1992, 33, 2204. (f) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Angew. Chem., Int. Ed. Engl. 1994, 33, 2204. (f) Giannini, L.; Solari, E.; Solari, E.; Solari, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1995, 117, 5801. (g) Black, D. G.; Swenson, D. C.; Jordan, R. F. Organometallics 1995, 14, 3539. (h) Blake, A. J.; Mountford, P.; Nikonov, G. I.; Swallow, D. Chem. Commun. 1996, 1835. (i) Schumann, H. Inorg. Chem. 1997, 36, 1103. (l) Martin, A.; Urhammer, R.; Gardner, T. G.; Jordan, R. F. Organometallics 1997, 24, 107, 382.

⁽³⁾ For calix[4]arenes, see: (a) Floriani, C. Chem. Eur. J. 1999, 5, 19. (b) Giannini, L.; Caselli, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgamellotti, A. J. Am. Chem. Soc. 1997, 119, 9198 and 9709. (c) Caselli, A.; Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. Organometallics 1997, 16, 5457. (d) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1998, 120, 437. (e) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1998, 120, 437. (e) Giannini, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1998, 120, 823. (f) Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1999, 121, 2784. (g) Giannini, L.; Guillemot, G.; Solari, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1999, 121, 2797. (h) Giannini, L.; Dovesi, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Angew. Chem., Int. Ed. 1999, 38, 807. (i) Castellano, B.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, A.; Rizzoli, C. Chem. Eur. J. 1999, 5, 722.

^{(4) (}a) Schrock, R. R. Acc. Chem. Res. **1997**, 30, 9. (b) Verkade, J. G. Coord. Chem. Rev. **1994**, 137, 233. (c) Duan, Z.; Verkade, J. G. Inorg. Chem. **1995**, 34, 5477, 4311, 1576. (d) Neuner, B.; Schrock, R. R. Organometallics **1996**, 15, 5. (e) Schrock, R. R.; Cummins, C. C.; Wilhelm, T.; Lin, S.; Reid, S. M.; Kol, M.; Davis, W. M. Organometallics **1996**, 15, 1470. (f) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. Organometallics **1996**, 15, 2777. (g) Nomura, K.; Schrock, R. R.; Davis, W. M. Inorg. Chem. **1996**, 35, 3695. (h) Freundlich, J. S.; Schrock R. R.; Davis, W. M. J. Am. Chem. Soc. **1996**, 118, 3643. (i) Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. Inorg. Chem. **1995**, 34, 4062. (j) Findeis, B.; Schubart, M.; Gade, L. H.; Möller, F.; Scowen, I.; McPartlin, M. M. J. Chem. Soc., Dalton Trans. **1996**, 125. (k) Aspinall, H. C.; Tillotsen, M. R. Inorg. Chem. **1996**, 35, 2163.

Communications

Complex 2, which represents the entry into the zirconium-porphodimethene organometallic chemistry, has been synthesized according to Scheme 1.8 The cis arrangement of the two chloride atoms is particularly appropriate for the metal functionalization, as was the case for a variety of other macrocyclic ancillary ligands such as tmtaa,² calix[4]arenes,^{3b} and porphyrins.⁶ The cis arrangement of the two chloride atoms is the consequence of the saddle shape conformation of the ligand having two sp³ and two sp² meso-carbons and with the metal 0.932(2) Å out of the N₄ plane.⁹ Particularly significant are the Zr…CH2 short contacts with two meso-ethyl groups, thus suggesting a structural intermediate in the metal-assisted aliphatic C-H activation (see below). The alkylation of $\frac{1}{2}$ led to the bis-alkyl derivatives, two of them, 3^{10} and 5, being isolated and characterized, while 4, which might not be isolated, led to the migration of one benzyl group to the monosubstituted meso-position,¹¹ thus forming the trianionic porphomethene ligand⁷ in complex **6**.¹² The structure of **6** (Figure 1)¹³ shows the $\eta^{1:}\eta^{1:}\eta^{5}$ bonding mode of

(6) For porphyrins, see: (a) Brand, H.; Arnold, J. Angew. Chem., Int. Ed. Engl. **1994**, 33, 95. (b) Brand, H.; Arnold, J. Organometallics **1993**, 12, 3655. (c) Kim, H.-J.; Whang, D.; Kim, K.; Do, Y. Inorg. Chem. **1993**, 32, 360. (d) Arnold, J.; Johnson, S. E.; Knobler, C. B.; Hawthorne, M. F. J. Am. Chem. Soc. 1992, 114, 3996. (e) Brand, H.; Arnold, J. J. Am. Chem. Soc. 1992, 114, 2266. (f) Brand, H.; Arnold, J. Coord. Chem. Am. Chem. Soc. 1992, 114, 2266. (f) Brand, H.; Arnold, J. Coord. Chem. Rev. 1995, 140, 137. (g) Aida, T.; Inoue, S. Acc. Chem. Res. 1996, 29, 39. (h) Kim, H.-J.; Jung, S.; Jeon, Y.-M.; Whang, D.; Kim, K. Chem. Commun. 1999, 1033. (i) Ryu, S.; Whang, D.; Kim, H.-J.; Kim, K.; Yoshida, M.; Hashimoto, K.; Tatsumi, K. Inorg. Chem. 1997, 36, 4607.
(d) Kim, H.-J.; Jung, S.; Jeon, Y.-M.; Whang, D.; Kim, K. Chem. Commun. 1997, 2201.

(7) Benech, J.-M.; Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C. Angew. Chem., Int. Ed. **1999**, *38*, 1957, and references therein.

(8) Procedure for 2. Solid ZrCl₄·THF₂ (5.57 g, 14.8 mmol) was added to a solution of 1 (9.41 g, 14.8 mmol) in toluene (600 mL) under argon atmosphere. The resulting solution was stirred at room temperature for 1 day. The undissolved white solid, LiCl, was filtered off, and the solution was evaporated to dryness. The residue was triturated with n-pentane to give a red powder (6.8 g, 72%), which was collected and dried in vacuo. Crystals suitable for X-ray analysis were obtained by The invacual crystal suitable for X-ray analysis were obtained by recrystallization in THF. Anal. Calcd for **2**, $C_{32}H_{38}N_4Cl_2$: C, 59.98; H, 5.98; N, 8.74. Found: C, 59.73; H, 6.16; N, 8.45. ¹H NMR (C₆D₆, 200 MHz, 298 K): δ 7.07 (d, J = 4.4 Hz, 4H, C₄H₂N); 6.26 (d, J = 4.4 Hz, 4H, C₄H₂N); 6.26 (d, J = 4.4 Hz, 4H, C₄H₂N); 2.66 (q, J = 7.32 Hz, 4H, CH₂); 2.43 (q, J = 7.32 Hz, 4H, CH₂); 1.92 (q, J = 7.32 Hz, 4H, CH₂); 1.15 (t, J = 7.32 Hz, 6H, CH₃); (0) Unumblished results

(9) Unpublished results.

(10) Procedure for 3. MeLi (42.9 mL, 1.51 M in Et₂O, 64.8 mmol) was added dropwise to a solution of 2 (20.82 g, 32.4 mmol) in toluene (600 mL) cooled to -30 °C. The resulting dark orange solution was warmed to room temperature, and the undissolved white solid, LiCl, was filtered off. The solution was evaporated to dryness, and *n*-pentane was added to give a brown powder (13.6 g, 70%), which was collected and dried in vacuo. Anal. Calcd for $C_{34}H_{44}N_4Zr$: C, 68.06; H, 7.39; N, 9.34. Found: C, 68.51; H, 6.89; N, 9.73. ¹H NMR (C₆D₆, 400 MHz, 298 K, ppm): δ 7.14 (d, J = 4.4 Hz, 4H, C₄H₂N); 6.44 (d, J = 4.4 Hz, 4H, C_4H_2N ; 2.73 (q. J = 7.3 Hz, 4H, CH₂); 2.27 (q. J = 7.3 Hz, 4H, CH₂); 2.03 (q. J = 7.3 Hz, 4H, CH₂); 1.18 (t. J = 7.3 Hz, 6H, CH₃); 0.94 (t. J7.3 Hz, 6H, CH₃); 0.9 (s, 6H, CH₃); 0.88 (t, J = 7.3 Hz, 6H, CH₃).

(11) Migration of the alkyl group from the metal to an electron-deficient imino group is known both for tmtaa (see ref 2) and for Schiffbase complexes: (a) Floriani, C.; Solari, E.; Corazza, F.; Chiesi-Villa, A.; Guastini, C. Angew. Chem., Int. Ed. Engl. **1989**, 28, 64. (b) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Chem. Soc., Dalton Trans. **1992**, 367. (c) Solari, E.; Maltese, C.; Latronico, M.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1998**, 2395.



Figure 1. View of compound 6 (hydrogens omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr1– η^5 (Pyr), 2.219(4); Zr1–N2, 2.257(7); Zr1–N3, 2.290(6); Zr1– N4, 2.188(7); Zr1-C40, 2.312(8); Zr1-O1, 2.453(5); C41-C40–Zr1, 129.8(6). η^5 (Pyr) indicates the centroid.

the tetrapyrrolic ligand and the η^1 bonding mode of the benzyl group. The migration of the second benzyl group was photochemically induced, thus forming 7, where zirconium is $\eta^5:\eta^1:\eta^5:\eta^1$ bonded⁵ to the *meso*-hexaethylbisbenzylporphyrinogen tetraanion. The bonding mode of the macrocyclic ligand in both 6 and 7 has been confirmed by the ¹H NMR spectra in solution and the X-ray analysis in the solid state.

The chemical evolution of 3 upon heating is completely different from that of 4. The reaction produced methane and led to the formation of Zr-C bonds with the α -carbons of the two meso-ethyl groups, as shown in complex $8.^{14}$ In the case of 3, we assume, as for the structure of 2, that the close geometrical proximity

Hz, 3H, CH₃); 0.68 (t, J = 7.34 Hz, 3H, CH₃). (13) Crystal data for **6**: C₅₀H₆₀N₄OZr, M = 824.24, monoclinic, space group $P2_1/n$, a = 18.880(2) Å, b = 11.940(2) Å, c = 19.253(2) Å, $\beta =$ $103.259(11)^\circ$, *V* = 4224.6(11)Å³, *Z* = 4, ρ_{calcd} = 1.296 g/mL, *F*(000) = 1744, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.302 mm⁻¹; crystal dimensions 0.24 × 0.16 × 0.10. Diffraction data were collected on a KUMA CCD at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on *F*² with all non-H atoms anisotropically defined. For 3071 observed reflections $[I > 2\sigma(I)]$ and 505 parameters, the conventional *R* is 0.0819 (wR2 = 0.2340 for 6996 independent reflections). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lens-field Road, Cambridge CB2 1EW (England). See the Supporting Information for more details.

⁽⁵⁾ For metal-porphyrinogen: (a) Floriani, C. *Pure Appl. Chem.* **1996**, *68*, 1. (b) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, J. Am. Chem. Soc. 1995, 117, 2805. (c) Isoz, S.; Floriani, C.; Schenk K.; Chiesi-Villa, A.; Rizzoli, C. Organometallics **1996**, *15*, 337. (d) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1995, 117, 2793. (e) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1092. (f) Jacoby, D.; Isoz, S.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, Organometallics 1995, 14, 4816. (g) Solari, G.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Organometallics **1997**, *16*, 508. (h) Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. J. Am. Chem. Soc. 1995, 117, 2793.

⁽¹²⁾ Procedure for $6.~(\rm PhCH_2)_2Mg$ (29.9 mL, 0.44 M in THF, 13.0 mmol) was added to a solution of 2 (8.35 g, 13.0 mmol) in toluene (350 mL) cooled to -30 °C. The reaction mixture was stirred at room temperature for 1 h and then was evaporated to dryness. Toluene (300 mL) was added, and the undissolved white solid, MgCl₂, was filtered off. The solution was evaporated to dryness, and the residue was treated with *n*-pentane to give a pink powder, which was collected and dried in vacuo (6.5 g, 61%). Crystals suitable for X-ray analysis were obtained by recrystallisation in THF/Et₂O. Anal. Calcd for 6, C₅₀H₆₀N₄: OZr: C, 72.86; H, 7.34; N, 6.80. Found: C, 72.45; H, 7.05; N, 6.34. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.28 (d, J = 4.4 Hz, 1H, C₄H₂N); 7.14 (m, 4H, ArH); 7.01 (d, J = 4.4 Hz, 1H, C₄H₂N overlapping with m, 2H, ArH); 6.75 (m, 1H, ArH); 6.53 (d, J = 4.4 Hz, 1H, C₄H₂N); 6.51 (d, J = 2.93 Hz, 1H, C_4H_2N); 6.50 (m, 3H, ArH); 6.40 (d, J = 2.93, 1H, C_4H_2N); 6.23 (d, J = 2.93 Hz, 1H, C_4H_2N); 6.22 (d, J = 4.4 Hz, 2H, $C_{4}H_2(N)$; 5.79 (d, J = 2.93, 1H, $C_{4}H_2(N)$; 4.13 (d, J = 13.2, 1H, CH₂Ph); 3.17 (s broad, 4H, THF); 3.49 (d, J = 13.2, 1H, CH₂Ph); 2.70 (q, J =



Figure 2. View of compound **9** (hydrogens omitted for clarity). Selected bond lengths (Å): Zr1-N1, 2.152(4); Zr1-N2, 2.194(4); Zr1-N3, 2.217(4); Zr1-N4, 2.152(4); Zr1-N5, 2.095(4); Zr1-C33, 2.624(5); Zr1-C34, 2.721(5); $Zr1-\eta^3(N5, C33, C34)$, 2.280(4); N5-C33, 1.387(6); C33-C34, 1.363(7). $\eta^3(N5, C33, C34)$ indicates the centroid.

between the methyl group and the CH₂ from two mesoethyl groups is crucial for the concerted elimination of CH₄ and the consequent metalation of the lateral ethyl chains. Unlike in the case of zirconium–porphyrinogen chemistry,^{5b} the metalation of the aliphatic chain is regiochemically selective; not only is the reaction occurring only at the α -carbon but also it produces a single stereoisomer. The absence of Zr····CH₂ (meso-ethyl) interactions prevented by the sterically more demanding benzyl subtituents in **4** opens the pathway of the nucleophilic attack by the benzylic carbanions to the meso-positions of the porphodimethene skeleton. The characterization of **8** included a quite preliminary X-ray analysis.⁹ The synthetic relevance of **8** has to be emphasized; it can be used as an intermediate in the

functionalization of the meso aliphatic chain of the porphodimethene skeleton, due to the easy demetalation, upon hydrolysis, of complexes of this type.^{5h} An additional interest in complex 8 comes from its potential use in the intermolecular C-H bond activation of hydrocarbons, as already reported for the Zr-porphyrinogen complexes.^{5a,b} The Zr-Me functionality in **3** has been engaged in other migration processes, exemplified by its reaction with Bu^tNC,¹⁵ which has some unusual peculiarities. The reaction led to the migration of both methyls to the isocyanide functionality and the intermediate formation of η^2 -C,N imine^{2f,3c} (see complex A in Scheme 1), which underwent a C-H (Me) deprotonation followed by a hydrogen transfer to one of the meso-positions. On the basis of the structural parameters, the deprotonated imine behaves more as an *N*-methylated enamine than as an azaallyl ligand (see complex **9** in Scheme 1^{16} and Figure 2^{17}), while the resulting porphomethene macrocycle displays an η^1 : η^1 : $\eta^1:\eta^1$ bonding mode proven by the X-ray structure of **9** and the NMR spectra in solution.

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Supporting Information Available: ORTEP drawings and tables giving crystal data and details of the structure determination, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **6** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990688S

(15) Durfee, L. D.; Rothwell, I. P. Chem. Rev. 1988, 88, 1059.

(16) Procedure for **9**. A solution of Bu^tNC (0.71 g, 8.5 mmol) in benzene (60 mL) was added dropwise to a dark orange solution of **3** (5.1 g, 8.5 mmol) in benzene (90 mL) cooled to -30 °C. The resulting dark violet solution was stirred at room temperature for 1 day and then evaporated to dryness. The residue was triturated with *n*-pentane to give a red powder (4.5 g, 77%), which was collected and dried in vacuo. Anal. Calcd for **9**, C₃₉H₅₃N₅Zr: C, 68.57; H, 7.82; N, 10.25. Found: C, 68.12; H, 7.35; N, 9.82. ¹H NMR (C₆D₆, 400 MHz, 298 K, ppm): δ 7.01 (d, J = 4.4 Hz, 2H, C₄H₂N); 6.39 (d, J = 3.4 Hz, 2H, C₄H₂N); 6.32 (d, J = 4.4 Hz, 2H, C₄H₂N); 6.13 (d, J = 3.4 Hz, 2H, C₄H₂N); 4.04 (s, 3H, CH₃); 2.51 (m, 4H, CH₂); 1.27 (g, J = 7.34 Hz, 4H, CH₂); 1.91 (m, 2H, CH₂); 1.10 (m, 6H, CH₂); 1.37 (s, 3H, CH₃); 1.36 (t, J = 7.34, 3H, CH₃); 1.11 (t, J = 7.34 Hz, 6H, CH₃); 0.89 (s, 9H, Bu¹); 0.61 (t, J = 7.34 Hz, 6H, CH₃); Crystal suitable for X-ray analysis were obtained from toluene/*n*-hexane.

(17) Crystal data for **9**. $C_{39}H_{53}N_5Zr$, M = 683.08, triclinic, space group $P\overline{1}$, a = 9.1942(8) Å, b = 10.9092(18) Å, c = 17.887(3) Å, $\alpha = 89.771(14)^\circ$, $\beta = 87.736(12)^\circ$, $\gamma = 71.089(13)^\circ$, V = 1695.9(4) Å³, Z = 2, $D_{calcd} = 1.338$ g/cm³, F(000) = 724, λ (Mo K α) = 0.71073 Å, μ (Mo K α) 0.360 mm⁻¹; crystal dimensions 0.28 × 0.20 × 0.15. Diffraction data were collected on a KUMA CCD at 143 K. The structure was solved with direct methods and refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. For 4681 observed reflections [I > $2\sigma(I)$] and 406 parameters, the conventional R is 0.0720 (wR2 = 0.1451 for 5140 indipendent reflections).

⁽¹⁴⁾ Procedure for **8**. MeLi (11.4 mL, 1.82 M in Et₂O, 20.8 mmol) was added dropwise to a solution of **2** (6.9 g, 10.4 mmol) in toluene (300 mL) at -30 °C. The resulting dark orange solution was stirred at room temperature for 1 h. The ¹H NMR showed that **2** was entirely converted into **3**. The solution was then heated at 110 °C for 2 h, and the undissolved white solid, LiCl, was filtered off. The solution was evaporated to dryness and the solid residue collected with *n*-pentane, yielding a brown powder (3.2 g, 55%). Anal. Calcd for **8**. C₃₂H₃₆N₄Zr: C, 67.68; H, 6.39, N, 9.86. Found: C, 68.08; H, 6.82, N, 9.55. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 6.45 (d, J = 3.91 Hz, 2H, C₄H₂N); 6.38 (d, J = 3.91 Hz, 2H, C₄H₂N); 5.95 (d, J = 3.91 Hz, 2H, C₄H₂N); 5.90 (d, J = 3.91 Hz, 2H, C₄H₂N); 5.18 (m, 4H, CH₂); 2.06 (q, J = 2.85 Hz, 2H, CH₂); 1.86 (q, J = 7.34 Hz, 4H, CH₂); 1.68 (d, J = 2.85 Hz, 6H, CH₃); 1.00 (t, J = 7.34 Hz, 6H, CH₃); 1.37 (s, 3H, CH₃); 0.88 (t, J = 7.34 Hz, 4Hz, CH₃); 5.95 (b, 2 = 0.5 Hz, 0.5 Hz,