Unsaturated 4,4'-bis-[5(4*H*)-oxazolones]: synthesis and evaluation of their *ortho*-palladation through C-H bond activation

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Abstract. Aromatic unsaturated 4,4'-bis-[5(4*H*)-oxazolones] have been prepared and their structural properties discussed. Metallation studies of these substrates towards palladium(II) acetate were also investigated.

Keywords: 4,4'-bis-[5(4*H*)-oxazolones]; metallation; ortho-palladation; C-H bond activation; pincer compounds

1. Introduction

C-H bond activation is the most important method for the synthesis of *ortho*-metallated complexes [1]. Nowadays, this reaction is extensively studied due to its synthetic possibilities for the functionalization of a large diversity of organic substrates [2].

Oxazolones are very important organic precursors and appropriate building blocks, which have attracted much attention due to their use as intermediates in pharmacology and for the synthesis of amino acids [3]. With numerous reactive sites, oxazolone scaffold allows for a large diversity of transformations such as stereoselective cycloadditions [4], opening of the heterocyclic ring [5], enantioselective alkylation [6] and arylations [7]. The *ortho*-metallation of 5(4*H*)-oxazolones is still a scarcely represented process. Our recent contributions have shown that unsaturated substrates can be regioselectively functionalized through *ortho*-palladation [8], and that metallated oxazolones may evolve through [2+2] photocycloaddition to give unprecedented oxazolones [9].

Following our current research on functionalization of unsaturated oxazolones [8,9], we have focused now our attention on bis-oxazolones. While the use of these substrates was limited to polymers [10], chain coupling reagents [11], and in pharmacology [12], the chemistry of these species, in particular unsaturated 4,4'-bis-[5(4*H*)-oxazolones], has been scarcely studied [13]. Moreover, no detailed structural information is available for 4,4'-bis-

[5(4*H*)-oxazolones].

In addition, the reactivity of unsaturated bis-oxazolones towards metallating agents is unknown. The only reported examples are limited to Pt and Pd coordination complexes of saturated 2,2'-bis-[5(4*H*)-oxazolones] [14]. However, as we have previously reported [8,9], the palladation approach could constitute the first step of an alternative synthetic strategy for reaching modified bis-oxazolones, which in turn are precursors for bis-amino acids, targets which have attracted significant interest in the last few years [15], but synthetically limited to classic organic transformations [16].

The interest to synthesize 4,4'-bis-[5(4*H*)-oxazolones] is increased by the potential use of these structures as multidentate ligands. For instance, some symmetrically substituted 4,4'-bis-[5(4*H*)-oxazolones] may be classified as pincer (NCN) ligands [1,17]. In this communication we describe the improved synthesis and structural characterization of 4,4'-bis-[5(4*H*)-oxazolones] and their reactivity towards metallating substrates as palladium(II) acetate.

2. Results and discussion

The unsaturated 4,4'-bis-[5(4*H*)-oxazolones] **2a**, **2b** [10b,18] and **2c** [18,19] were prepared according to literature procedures (Equation 1). Benzenedicarboxaldehydes (**1a-c**) were reacted with hippuric acid using Erlenmeyer conditions to afford *ortho*-, *meta*- and *para*-substituted (*Z,Z'*)-2,2'-diphenyl-4,4'-phenylenedimethylene-bis-5[(4*H*,4'*H*)-oxazolones] **2a-c** in moderate to good yields.

Equation 1

Although two geometric isomers are possible for **2a-c**, the Erlenmeyer reaction favors the thermodynamically more stable *Z* isomer, which is easily isolated by recrystallization [8]. The structure and the correct geometry for **2a-c** were inferred from spectroscopic (IR, NMR), MS, X-ray and elemental analyses data. The structures of the unsaturated 4,4'-bis-[5(4*H*)-oxazolones] **2a-c** are drawn in Chart 1.

The IR spectra of **2a-c** exhibit strong carbonyl stretching vibration bands around $\nu = 1785\text{ cm}^{-1}$, while the absence of any band assignable for carboxylic OH or amidic NH function supports the formation of heterocyclic system. The NMR data fully agree with the assigned configurations. Only one set of signals is present on each spectrum, showing the presence of only one isomer in solution. The pattern of signals shows that the two oxazolone units are chemically equivalent, meaning that the molecule is symmetric with respect to the central C_6H_4 ring. We assume that the configuration around the $\text{C}=\text{C}$ double bond is the thermodynamic *Z*-isomer, as shown in Chart 1, by analogy of the synthetic method here employed with previously reported syntheses of *Z*-oxazolones. This assumption will be confirmed through the determination of the crystal structure of **2c**.

Chart 1

The structure of (Z,Z')-2,2'-diphenyl-4,4'-*p*-phenylene-dimethylene-bis-5[(4*H*,4'*H*)-oxazolone] (**2c**) was determined by X-ray diffraction methods. Crystals of **2c**·C₆H₅Me suitable for X-ray measurements were obtained after recrystallization from toluene (**Fig. 1**).

Fig. 1.

2c crystallizes in the triclinic system, space group P-1, with two centrosymmetric molecules in the unit cell, together with two toluene molecules. The molecular structure displays a ZZ configuration about the C9C10 and C17C18 double bonds, as expected. In addition, if we look along the axis C17-C14-C11-C10 and perpendicularly to the plane containing the phenylene unit we observe the *E* orientation of the two azlactone rings. In comparison with previously determined (Z)-2-phenyl-4-arylidene-5(4*H*)-oxazolones, which are planar [20], the introduction of a second oxazolone ring resulted in a partial loss of planarity. The value of the dihedral angle between the plane of phenylene and the plane containing the aromatic ring (C3-C8) is 16.24(4)° while that of the phenylene with the plane containing the other terminal aromatic ring (C21-C26) is 14.67(4)°. This fact induces a slight helicity of the system.

The molecular configuration of **2c** is stabilized by several intermolecular hydrogen bonds. A closer check of the crystal structure revealed C-H...O intermolecular interactions involving O1 and O3 atoms from the oxazolone rings [C17-H17...O1 2.6702(19) Å, C12-H12...O1 2.7585(22) Å, C6-H6...O3 2.7022(24) Å and C10-H10...O3 2.6515(19) Å] (**Fig. 2** top). Further stabilization of **2c** in the solid state results from the formation of a dimeric structure

in which two bis-oxazolones are connected by π - π interactions: tilted edge-to-face and offset face-to-face. Tilted edge-to-face interactions are given by the aromatic rings of toluene molecules which are parallel and quasi perpendicular on the other aromatic rings (**Fig. 2** top). Each aromatic ring belonging to toluene has two edge tilted to face interactions (on both sides) with the terminal aromatic rings of two bis-oxazolone molecules in edge tilted to face arrangements. The distances between the centroid of the toluene aromatic ring and the contact hydrogens are 2.9925 (3) Å and 2.7213 (2) Å respectively. The latter interactions are given by the aromatic rings of two superposed bis-oxazolones, the distance between the ring centroids from phenyls centroids is 3.75396 (6) Å suggesting the existence of weak offset face-to-face interactions (**Fig 2** bottom). The same interactions were noticed between the phenylene centroids 3.5578 (6) Å.

Fig. 2.

Following our aim to study the metallating behavior of bis-oxazolones, ligands **2a-c** were reacted with Pd(OAc)₂ using our previously optimized conditions [9]. Under these conditions (CF₃COOH, 70 °C), neither **2a** nor **2c** gave characterizable species, the products separated after workup having very low solubility in deuterated solvents. In the case of **2a** the only evidence for the formation of a palladated product was the MALDI mass spectrum, since peaks of ions corresponding to [2aPd]⁺ were detected with a high abundance at *m/z* 524.8 amu.

However, when **2b** was treated in the same conditions as **2a** or **2c**, the C-H bond activation occurs easily and the pincer compound **3** was isolated in 86% yield after crystallization from dichloromethane/hexane (**Equation 2**). It is to be noted that due to its symmetrical structure, with two donor nitrogen atoms and a central ligating C atom **2b** classifies as a NCN pincer ligand [17]. The increase interest to synthesize pincer complexes

refers not only to their numerous applications in asymmetric synthesis [21], catalysis [22] but also to the big variety of transformations in which these compounds are involved [23]

Equation 2

The ^1H and ^{13}C NMR spectra are consistent with the symmetrical structure, and show sharp signals due to the presence of a single species. The deshielded signal attributed to $\text{H}_{2''}$ in **2b** is not longer seen on the ^1H NMR spectrum of **3**, giving unambiguous proof of the metallation. The vinylic protons of the benzylidene fragment $\text{H}_{7''}$, which are equivalent and appear as a singlet, shift downfield from 7.32 ppm in **2b** to 7.66 ppm in **3**. Full assignments of all resonances in **3** were made using NOESY-1D experiments. The selective saturation of the signal at 7.66 ppm (assigned to $\text{H}_{7''}$) induces a clear NOE effect on the signal at 7.48 ppm (assigned to the $\text{H}_{6''}$ proton of the *ortho*-palladated ring). On the other hand, the selective saturation of the signal at 7.32 ppm (assigned to $\text{H}_{5''}$) gives a clear NOE with the doublet at 7.48 ppm ($\text{H}_{6''}$), showing unambiguously the formation of the *ortho*-palladated unit. The presence of trifluoroacetate anion has been confirmed by ^{19}F NMR spectroscopy, the two broad singlet peaks at -75.78 and -76.44 ppm indicating a dynamic structure at room temperature. Therefore, the whole molecule shows two different behaviors on the NMR time scale. The pincer ligand displays a static behavior, giving sharp and well resolved signals, while the trifluoroacetate is involved on a dynamic process, likely its coordination and decoordination. This dynamic process seems to be closely related with the high steric hindrance exerted by the two phenyl groups of the oxazolone at 2,2' positions. To further confirm the formation of a monomeric structure we have used MALDI to detect palladacycle species. The spectrum of **3** exhibits only the ion corresponding to the $[\text{M-TFA}]^+$ fragment at m/z 524.8.

It is worthy of note that the formed palladacycle **3** has two six-membered fused

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metallacycles. These pincer complexes are formed to a lesser extent than five-membered ones [17], show increased catalytic efficiency [24] and they are limited to few examples [25].

Taken together these results demonstrate that some unsaturated 4,4'-bis-[5(4*H*)-oxazolones] can be metallated. We believe that the simple case presented herein will open the way to a whole new series of metallated compounds which may be used in catalytic studies and in preparation of bis-amino acids. The synthesis of more complex bis-oxazolonic substituted substrates as well as use of different transition metals is currently under investigation in our laboratories.

3. Experimental

3.1. Materials

The unsaturated oxazolones **2b** and **2c**, were already synthesized but an entirely spectroscopic characterization is missing and therefore a fully characterization is given here.

3.2. Physical methods

Chemicals of commercial grade were used without further purification. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 , at room temperature, on a Bruker Avance 400 spectrometer (δ in ppm, J in Hz) at ^1H operating frequency of 400.13 MHz. ^1H and ^{13}C NMR spectra were referenced using the solvent signal as internal standard. MALDI mass spectra were recorded on a MALDI-TOF Microflex (Bruker) spectrometer from CHCl_3 solutions (DCTB as matrix). Infrared spectra ($4000\text{--}380\text{ cm}^{-1}$) were recorded on a Perkin-Elmer Spectrum One IR spectrophotometer, using nujol mulls between polyethylene sheets. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser.

3.3. Synthesis of compounds

3.3.1. Preparation of (*Z,Z'*)-2,2'-diphenyl-4,4'-o-phenylenedimethylene-bis-[5(4*H*,4'*H*)-oxazolone] (**2a**)

Benzene-1,2-dicarboxaldehyde (0.595 g, 4.435 mmol), *N*-benzoylglycine (1.590 g, 8.871 mmol), anhydrous sodium acetate (0.728 g, 8.871 mmol) and acetic anhydride (2.720 g, 26.615 mmol) were added in a 100 mL round-bottomed flask. The mixture was heated for two hours at 100 °C and then allowed to cool at room temperature. The precipitate was washed with ethanol, cooled down for 30 minutes and then filtered. **2a** was obtained as an yellow solid after recrystallization from ethanol (Yield 0.783 g, 42%). ^1H NMR (CDCl_3) δ ppm: 7.54 (t, $^3J = 7.6\text{ Hz}$, 4H, $2\text{H}_{3'}$, 2H_5), 7.59-7.66 (m, 4H, $2\text{H}_{4'}$, $\text{H}_{4''}$, $\text{H}_{5''}$), 7.70 (s, 2H, $2\text{H}_{7''}$),

8.19 (d, $^3J = 7.2$ Hz, 4H, 2H₂, 2H₆), 8.79 (m, 2H, H₃^{''}, H₆^{''}). ¹³C{¹H} NMR (CDCl₃) δ ppm: 125.32 (2C, C₁[']), 126.59 (2C, C₇[']), 128.59 (4C, 2C₂['], 2C₆[']), 129.03 (4C, 2C₃['], 2C₅[']), 130.83 (2C, C₄[']), 132.65 (2C, C₃^{''}, C₆^{''}), 133.74 (2C, C₄^{''}, C₅^{''}), 134.01 (2C, C₁^{''}, C₂^{''}), 134.91 (2C, C₂), 161.25 (2C, C₁), 167.04 (2C, C₃). MS (MALDI +) *m/z*, (rel. int. %): 420.1 (98.5%) [M]⁺. IR: ν = 1792 cm⁻¹ (C=O), 1639 cm⁻¹ (C=N). Anal. Calc. for C₂₆H₁₆N₂O₄ (420.11): C, 74.28; H, 3.84; N, 6.66. Found: C, 74.55; H, 3.67; N, 6.74.

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3.3.2. Preparation of (Z,Z')-2,2'-diphenyl-4,4'-m-phenylenedimethylene-bis-5[(4H,4'H)-oxazolone] (2b)

Benzene-1,3-dicarboxaldehyde (1.650 g, 12.301 mmol), *N*-benzoylglycine (4.410 g, 24.602 mmol), anhydrous sodium acetate (2.018 g, 24.602 mmol) and acetic anhydride (7.530 g, 73.808 mmol) were added in a 100 mL round-bottomed flask. The mixture was heated for two hours at 100 °C and then allowed to cool at room temperature. The precipitate was washed with ethanol, cooled down for 30 minutes and then filtered. **2b** was obtained as a yellow solid after recrystallization from EtOH (Yield 4.290 g, 83%). ¹H NMR (CDCl₃) δ ppm: 7.32 (s, 2H, H₇^{''}), 7.49 (t, $^3J = 7.8$ Hz, 4H, 2H₃['], 2H₅[']), 7.52-7.70 (m, 3H, 2H₄['], H₅[']), 8.19 (d, $^3J = 7.2$ Hz, 4H, 2H₂['], 2H₆[']), 8.33 (d, $^3J = 8.1$ Hz, 2H, H₄^{''}, H₆^{''}), 9.00 (s, 1H, H₂^{''}). ¹³C{¹H} NMR (CDCl₃) δ ppm: 125.28, 134.12, 134.17 (3C, C₁^{''}, C₁['], C₂), 128.54 (4C, 2C₂['], 2C₆[']), 128.96 (4C, 2C₃['], 2C₅[']), 129.49 (1C, C₅^{''}), 130.61 (2C, 2C₇[']), 133.57 (2C, C₄[']), 134.49 (2C, C₄^{''}, C₆^{''}), 136.00 (1C, C₂^{''}), 164.12 (1C, C₁), 167.45 (1C, C₃). MS (MALDI +) *m/z*, (rel. int. %): 420.1 (46.8%) [M]⁺. IR: ν = 1789 cm⁻¹ (C=O), 1647 cm⁻¹ (C=N). Anal. Calc. for C₂₆H₁₆N₂O₄ (420.11): C, 74.28; H, 3.84; N, 6.66. Found: C, 74.22; H, 3.62; N, 6.93.

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3.3.3. Preparation of (Z,Z')-2,2'-diphenyl-4,4'-p-phenylenedimethylene-bis-5[(4H,4'H)-oxazolone] (2c)

Benzene-1,4-dicarboxaldehyde (0.963 g, 7.179 mmol), *N*-benzoylglycine (2.570 g, 14.359 mmol), anhydrous sodium acetate (1.178 g, 14.359 mmol) and acetic anhydride (1.178 g, 14.359 mmol) were added in a 100 mL round-bottomed flask. The mixture was heated for two hours at 100 °C and then allowed to cool at room temperature. The precipitate was washed with ethanol, cooled down for 30 minutes and then filtered. **2c** was obtained as a yellow solid after recrystallization from ethanol (Yield 2.354 g, 78%). ¹H NMR (400 MHz, *CDCl*₃) δ ppm: 7.26 (s, 2H, 2H_{7''}), 7.57 (t, ³*J* = 7.3 Hz, 4H, 2H_{3'}, 2H_{5'}), 7.65 (t, ³*J* = 7.4 Hz, 2H, 2H_{4'}), 8.23 (d, ³*J* = 7.2 Hz, 4H, 2H_{2'}, 2H_{6'}), 8.32 (s, 4H, 2H_{2''}, H_{3''}, H_{5''}, H_{6''}). ¹³C{¹H} NMR (*CDCl*₃) δ ppm: 125.39, 134.62, 135.83 (6C, 2C_{1'}, 2C_{2'}, C_{1''}, C_{4''}), 128.57 (4C, 2C_{2''}, 2C_{6'}), 129.03 (4C, 2C_{3'}, 2C_{5'}), 130.06 (2C, 2C_{7''}), 132.65 (4C, C_{2''}, C_{3''}, C_{5''}, C_{6''}), 133.69 (2C, C_{4'}), 162.23 (2C, C₁), 167.35 (2C, C₃). MS (MALDI +) *m/z*, (rel. int. %): 420.1 (5.6%) [*M*]⁺. IR: ν = 1785, 1764 cm⁻¹ (C=O), 1650 cm⁻¹ vs (C=N). Anal. Calc. for C₂₆H₁₆N₂O₄ (420.11): C, 74.28; H, 3.84; N, 6.66. Found: C, 74.42; H, 3.98; N, 6.41.

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3.3.4. Preparation of (3)

To a stirred solution of **2b** (0.295 g, 0.701 mmol) in TFA (5 mL), palladium acetate (0.315 g, 1.403 mmol) was added. The solution was refluxed at 70 °C for 2 hours and the mixture was then treated with water. The precipitate formed was filtered and washed several times with water to remove the acid. After complete dryness the solid was dissolved in CH₂Cl₂ and the precipitated with hexane to afford **3** as a yellow solid (Yield 0.386 g, 86%). ¹H NMR (400 MHz, *CDCl*₃) δ ppm: 7.32 (t, ³*J* = 7.4 Hz, 1H, H_{5''}), 7.42-7.51 (m, 6H, 2H_{3'}, 2H_{5'}, H_{4''}, H_{6''}), 7.59 (t, ³*J* = 7.6 Hz, 2H, 2H_{4'}), 7.66 (s, 2H, 2H_{7''}), 8.21 (d, ³*J* = 7.5 Hz, 4H, 2H_{2'}, 2H_{6'}). ¹³C{¹H} NMR (*CDCl*₃) δ ppm: 122.10, 126.09, 135.05, 139.10 (4C, C_{1'}, C_{1''}, C_{2'}, C_{2''}), 126.59 (1C, C_{5''}), 128.81 (4C, 2C_{3'}, 2C_{5'}), 130.61 (4C, 2C_{2'}, 2C_{6'}), 135.09 (2C, C_{4''}, C_{6''}), 135.57 (2C, 2C_{4'}), 138.14 (2C, C_{7''}), 160.34 (2C, C₁), 169.25 (2C, C₃). ¹⁹F NMR (376 MHz, *CDCl*₃) δ ppm: -76.44, -75.78 (broad s, 3F). MS (MALDI +) *m/z*, (rel. int. %): 524.8 (100%) [*M*-CF₃COO]⁺.

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IR: ν = 1804, 1791 cm^{-1} vs (C=O), 1650, 1635 cm^{-1} vs (C=N). Anal. Calc. for $\text{C}_{28}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_6\text{Pd}$ (637.99): C, 52.64; H, 2.37; N, 4.39. Found: C, 52.87; H, 2.43; N, 4.56.

3.4. Crystal structure determination

Data collection was performed at room temperature on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo-K α radiation (λ = 0.71073 Å). An hemisphere of data was collected based on three ω -scan or ϕ -scan runs. The diffraction frames were integrated using the program CrysAlis RED [26] and the integrated intensities were corrected for absorption with SADABS [27]. The structure was solved and developed by Patterson and Fourier methods [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structure was refined to F_o^2 , and all reflections were used in the least-squares calculations [29].

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Equation 1 Reagents and conditions: Ac_2O , NaOAc , 100°C , 2h; **2a** (42%), **2b** (83%), **2c** (78%)

Chart 1

Fig. 1. ORTEP plot of **2c** with thermal ellipsoids drawn at the 50% probability level

Fig. 2. Diamond view of intermolecular interactions in **2c**

Equation 2 Reagents and conditions: Pd(OAc)_2 , $\text{CF}_3\text{CO}_2\text{H}$, 70 °C, 2h; (86%)

References

- [1] (a) J. Dupont, M. Pfeffer (Eds.), *Palladacycles: Synthesis, Characterization and Applications*, Wiley-VCH: Weinheim, Germany, 2008;
- (b) K. Godula, D. Sames, *Science* 312 (2006) 67;
- (c) D. Alberico, M.E. Scott, M. Lautens, *Chem. Rev.* 107 (2007) 174;
- (d) X. Chen, K.M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem., Int. Ed.* 48 (2009) 5094;
- (e) R. Giri, B.F. Shi, K.M. Engle, N. Maugel, J.Q. Yu, *Chem. Soc. Rev.* 38 (2009) 3242;
- (f) D.A. Colby, R.G. Bergman, J.A. Ellman, *Chem. Rev.* 110 (2010) 624;
- (g) F. Bellina, R. Rossi, *Chem. Rev.* 110 (2010) 1082.
- [2] (a) K.L. Hull, M.S. Sanford, *J. Am. Chem. Soc.* 131 (2009) 9651;
- (b) L.C. Campeau, D.J. Schipper, K. Fagnou, *J. Am. Chem. Soc.* 130 (2008) 3266;
- (c) K.L. Hull, M.S. Sanford, *J. Am. Chem. Soc.* 129 (2007) 11904;
- (d) D. Shabashov, O. Daugulis, *Org. Lett.* 8 (2006) 4947;
- (e) H. Zhou, W.-J. Chung, Y.-H. Xu, T.-P. Loh, *Chem. Commun.* (2009) 3472;
- (f) H. Zhou, Y.-H. Xu, W.-J. Chung, T.-P. Loh, *Angew. Chem., Int. Ed.* 48 (2009) 5355;
- (g) M. Yamashita, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* 11 (2009) 2337;
- (h) M. Murai, K. Miki, K. Ohe, *Chem. Commun.* (2009) 3466;
- (i) K.L. Hull, M.S. Sanford, *J. Am. Chem. Soc.* 131 (2009) 9651.
- [3] C. Cativiela, M.D. Díaz-de-Villegas, in: D. C. Palmer (Ed.), *The Chemistry of Heterocyclic Compounds*, Wiley, New York, 2004, vol. 60, pp. 129-330.
- [4] A. Avenoza, J.H. Busto, C. Cativiela, J.M. Peregrina, *Tetrahedron Lett.* 43 (2002) 4167.
- [5] (a) G.-D. Roiban, T. Soler, M. Contel, I. Grosu, C. Cativiela, E.P. Urriolabeitia, *Synth. Commun.* DOI: 10.1080/00397911.2010.523157;
- (b) B.S. Jursic, S. Sagiraju, D.K. Ancalade, T. Clark, E.D. Stevens, *Synth. Commun.* 37 (2007) 1709;

Con formato: Español (alfab. internacional)

(c) N. Gagey, M. Emond, P. Neveu, C. Benbrahim, B. Goetz, I. Aujard, J.B. Baudin, L. Jullien, Org. Lett. 10 (2008) 2341.

[6] (a) B.M. Trost, X. Ariza, J. Am. Chem. Soc. 121 (1999) 10727;

(b) B.M. Trost, C. Jakel, B. Plietker, J. Am. Chem. Soc. 125 (2003) 4438.

[7] X.X. Liu, J.F. Hartwig, Org. Lett. 5 (2003) 1915.

[8] G.-D. Roiban, E. Serrano, T. Soler, M. Contel, I. Grosu, C. Cativiela, E.P. Urriolabeitia, Organometallics 19 (2010) 1428.

Con formato: Español (alfab. internacional)

[9] D. Roiban, E. Serrano, T. Soler, I. Grosu, C. Cativiela, E.P. Urriolabeitia, Chem. Commun. (2009) 4681.

[10] (a) L.D. Taylor, T.E. Platt, M.H. Mach, J. Polymer Sci. B Polymer Lett. 8 (1970) 537;

(b) M. Ueda, K. Kino, Y. Imai, J. Polymer Sci. Polymer Chem. Ed. 13 (1975) 659.

[11] M. Acevedo, A. Fradet, J. Polym. Sci., Part A: Polym. Chem. 31 (1993) 1579.

[12] A. Mustafa, A.H.E. Harhash, M. Kamel, J. Am. Chem. Soc. 77 (1955) 3860.

[13] (a) C. Cativiela, M.D. Diaz de Villegas, P. Ferrer, J.I. Garcia, Trends in Het. Chem. 3 (1993) 31;

Con formato: Español (alfab. internacional)

(b) J.K. Rasmussen, S.M. Heilmann, L.R. Krepski, in: Encyclopedia of Polymer Science and Engineering, 2nd edn., John Wiley & Sons, New York, 1988, vol. 11, pp. 558-571;

(c) A.S. Girgis, M. Ellithy, Bioorgan. Med. Chem. 14 (2006) 8527;

(d) W. Bauer, K. Polborn, W. Beck, J. Organomet. Chem. 579 (1999) 269;

(e) A.H.M. Elwahy, A.A. Abbas, Y.A. Ibrahim, J. Chem. Research (S) (1998) 184.

[14] M. Prem, W. Bauer, K. Polborn, W. Beck, Z. Naturforsch., B: Chem. Sci. 53 (1998) 965.

[15] (a) S. Schumann, K. Zeitler, M. Jager, K. Polborn, W. Steglich, Tetrahedron 56 (2000) 4187;

(b) G.B. Hoven, J. Efskind, C. Romming, K. Undheim, J. Org. Chem. 67 (2002) 2459.

[16] (a) F. Paradisi, G. Porzi, S. Rinaldi, S. Sandri, Tetrahedron Asymmetry 11 (2000) 1259;

(b) A.-S. Carlstrom, T. Frejd, J. Org. Chem. 56 (1991) 1289.

- [17] D. Morales-Morales, C.M. Jensen, *The Chemistry of Pincer Compounds*, Elsevier, Amsterdam, 2007.
- [18] P. Ruggli, O. Schetty, *Helv. Chim. Acta*, 23 (1940) 718.
- [19] M. Ahmed, H. Abdel, H. Elsayed, K. Mohamed, *J. Am. Chem. Soc.* 77 (1955) 3860.
- [20] (a) P.P. Haasbroek, D.W. Oliver, A.J.M. Carpy, *J. Mol. Struct.* 648 (2003) 61;
(b) V. Busetti, J.A. Mayoral, C. Cativiela, M.D. Diaz de Villegas, D. Ajo, *Z. Kristallogr.* 189 (1989) 65.
- [21] H. Nishiyama, *Chem. Soc. Rev.* 36 (2007) 1133.
- [22] K.J. Szabo, *Synlett* (2006) 811.
- [23] (a) J.I. van der Vlugt, *Angew. Chem., Int. Ed.* 49 (2010) 252;
(b) J.M. Serrano-Becerra, D. Morales-Morales, *Curr. Org. Synth.* 6 (2009) 169;
(c) J.T. Singleton, *Tetrahedron* 59 (2003) 1837.
- [24] M.S. Yoon, D. Ryu, J. Kim, K.H. Ahn, *Organometallics* 25 (2006) 2409.
- [25] (a) A. Naghipour, S.J. Sabounchei, D. Morales-Morales, D. Canseco-Gonzalez, C.M. Jensen, *Polyhedron* 26 (2007) 1445;
(b) A.J. Canty, N.J. Minchin, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (1987) 1477;
(c) C. Seward, W.L. Jia, R.Y. Wang, S. Wang, *Inorg. Chem.* 43 (2004) 978;
(d) S. Das Adhikary, T. Samanta, G. Roymahapatra, F. Loiseau, D. Jouvenot, S. Giri, P.K. Chattaraj, J. Dinda, *New J. Chem.* 34 (2010) 1974.
- [26] Oxford Diffraction. CrysAlis RED. version 1.171.27p8. 2005, release CrysAlis171 .NET, Abingdon, Oxford, England.
- [27] Sheldrick, G. M. SADABS, 2008, University of Göttingen, Germany.
- [28] Sheldrick, G. M. SHELXS-86, *Acta Crystallogr. A* 46 (1990) 467.
- [29] Sheldrick, G. M. SHELXL-97: FORTRAN program for the refinement of crystal structures from diffraction data. Göttingen University, 1997. Molecular graphics were S23 done using

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