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Synthesis of palladium–biscarbene complexes derived from 1,1′-methylenebis(1,2,4-triazole) functionalized in the methylene bridge

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Abstract

Palladium–biscarbene complexes derived from *N*,*N*′-bis(1,2,4-triazol-1-yl)methane, which bear an alkyl chain functionalized with a hydroxyl group, have been synthesized ([Pd(L1)Br_2] (**6**) and [Pd(L1)I_2] (**7**) [L1 = 1,1′-(3-hydroxypropylidene)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)]). Each product is obtained as a non-equimolecular mixture of two conformers. The hydroxyl group has been replaced by bromide and methanesulphonate and ([Pd(L2)Br_2] [L2 = 1,1′-(3-bromopropylidene)bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)] (**9**)) and ([Pd(L3)Br_2] [L3 = 1,1′-(3-methanesulphonyloxypropylidene)-bis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene)] (**10**)) were obtained, respectively, as mixtures of conformers. All compounds consist of a six-membered metallacyclic structure in a boat conformation. Major conformers present the functionalized chain in the axial position, while in minor conformers it is located in the equatorial position.

Keywords: Palladium; Carbenes; Metallacycles; 1,2,4-Triazole; Hydroxyl; Bromide; Methanesulphonate

1. Introduction

N-Heterocyclic carbenes (NHCs) derived from imidazole have been widely used to coordinate transition metals and the resulting complexes have proven to have a great number of catalytic applications [1]. NHCs derived from imidazole are the most popular carbenes although some NHC systems derived from 1,2,4-triazole have been prepared and used as catalysts [1a,1h,2].

Due to the increased interest in designing efficient synthetic methods that are environmentally benign, the development of recyclable immobilized catalysts is an interesting goal. Very few examples have been reported of catalysts based on NHC that have been immobilized; one such example is a pincer-biscarbene-complex of Pd that was immobilized on clay through adsorption or cationic exchange [3]. The preparation of polymers or dendrimers containing this kind of complex requires the NHCs or their precursors to have one functional group. A number of functionalized NHC-complexes [4–7] or salt precursors of NHC [8,9] have been synthesized and these were bonded to a polymer or silica. Other complexes bearing NHC have been immobilized on a polymer or dendrimer through the use of a ligand other than the NHC system [10]. Biscarbenes derived from

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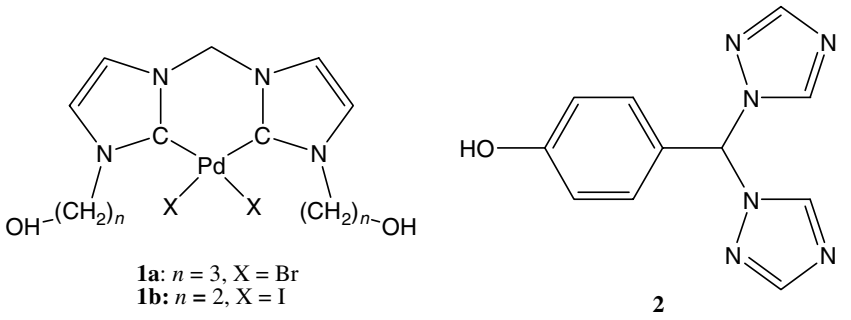


Fig. 1. Chemical structures of the previously described compounds **1** and **2**.

N,*N*′-diimidazolylmethane bearing a hydroxyalkyl group at each nitrogen atom **1** (Fig. 1) were obtained by Herrmann and were attached to polystyrene [11]. In 2002, we reported a derivative of *N*,*N*′-bis(1,2,4-triazol-1-yl)methane (**2**) (Fig. 1) that has a hydroxyphenyl group attached to the methylene unit and this compound was used in the synthesis of an NHC-containing generation zero dendrimer [12]. In this case the carbene moieties were obtained in the last step and we were unable to prepare the functionalized biscarbene-complex with **2** before coupling to the core. In fact, release of the heterocycles was observed upon quaternization of **2** – probably due to the significant electrophilic character of the benzyl methyne of the double salt [13].

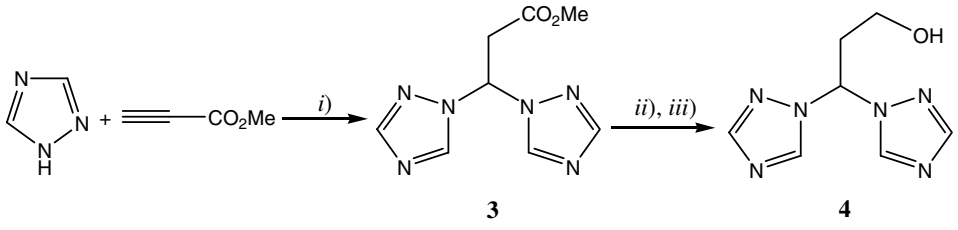
A biscarbene derived from 1,3-bis(*N*-imidazol-1-yl)propane functionalized with a hydroxyl group in the bridge was prepared by Arnold et al. [14].

We report here the synthesis of several biscarbene complexes derived from *N*,*N*′-bis(1,2,4-triazol-1-yl)methane functionalized on the methylene bridge with a hydroxyalkyl group as well as the corresponding bromide and mesylate derivatives. In these complexes the presence of a benzyl methyne is avoided.

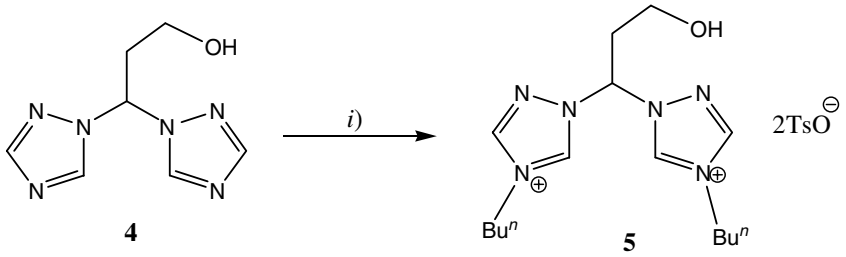
2. Results and discussion

In previous papers we described the synthesis of ester **3** by a double Michael addition [15] and this compound was subsequently reduced to alcohol **4** [16] (Scheme 1). These compounds represent two new examples of *N*,*N*′-bis(1,2,4-triazol-1-yl)methanes functionalized in the methylene bridge. In these two examples a benzylic methyne is not present. The two N4 atoms of the alcohol **4** were quaternized by reaction with a large excess of butyl tosylate at 100 °C and the corresponding salt **5** was obtained (Scheme 2).

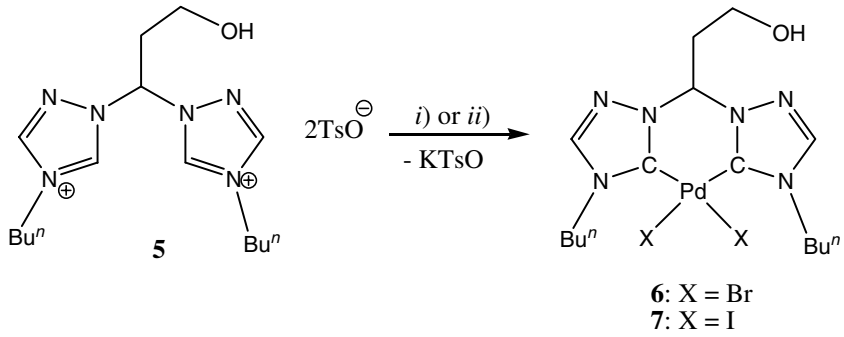
The release of heterocycles was not observed, which confirms that the benzylic methyne is responsible for the low stability of the double salt obtained from **2**.



Scheme 1. (i) NaH, THF, reflux, (ii) $LiAlH_4$, THF, −60 °C, (iii) H_2O, −60 °C.



Scheme 2. (i) *n*-BuOTs, 100 °C, 24 h.



Scheme 3. (i) $Pd(OAc)_2$, KBr, THF, DMSO, r.t., 1 h. (ii) $Pd(OAc)_2$, KI, THF, 0 °C, 24 h.

^{1}H NMR spectra confirm the formation of the **5** by the appearance of signals corresponding to butyl and tosylate moieties and the shift to lower field of the signals corresponding to H3 (9.42 ppm) and H5 (10.59 ppm) [13].

Reaction of the salt **5** with palladium(II) acetate in the presence of potassium bromide or iodide gave the biscarbene–palladium complexes $[Pd(L1)Br_2]$ (**6**) and $[Pd(L1)I_2]$ (**7**) (Scheme 3), each of which was obtained as a mixture of two compounds in an 8:1 ratio (determined by ^{1}H NMR spectroscopy in DMSO-d_6). It was not possible to separate the compounds and no variation in the relative ratios was observed after successive crystallization of the mixtures. This observation indicates the possibility of an interchange between the two compounds at room temperature through slow equilibria on the NMR time scale.

All of the compounds obtained give rise to a ^{1}H NMR pattern similar to that observed for 1,1′-methylenebis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) (**8**) [2a] (Fig. 2), apart from the 2-hydroxyethyl groups and the CH of the metallacyclic rings.

Both major compounds of **6** and **7** (Scheme 3) show the same ^{1}H NMR spectrum and they are very similar to those of the minor compounds, whose spectra are identical. The absence of a signal due to H5 of the triazole ring and the presence of a singlet due to H3 of the same heterocycle (at 8.92 ppm for the major compounds and 8.88 ppm for the minor compounds) are indicative of biscarbene formation. The most marked differences between the spectra of the major and minor compounds are in the signals corresponding to the 2-hydroxyethyl groups and, in particular, the chemical shifts of the CH protons of the metallacyclic ring. These latter signals appear as triplets at 6.79 ppm for the major compounds and 7.12 ppm for the minor components. Formation of the carbene was confirmed by ^{13}C NMR spectroscopy. The carbene carbon signals of the two major compounds are observed at 163.8 and 167.9 ppm, respectively [2a] (signals for the carbene carbons of the minor compounds could not be observed due to the small quantities present). All of the observations outlined above are consistent with the major and minor compounds in both mixtures being isomers. The existence of equilibria between these compounds was confirmed by NOESY-ID [17].

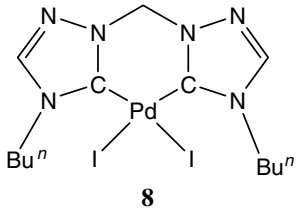


Fig. 2. The previously reported compound **8**.

Similarly to observed with palladium complexes bearing diphosphine ligands [18], at high temperature (363 K for **6** and 380 K for **7**) the signals are broadened and the chemical shifts of the CH protons of the metallacyclic ring are close to coalescence (Fig. 3). The coalescence of these signals has been observed at 378 K for **6** and 421 K for **7**. At higher temperatures the equilibriums became fast on the NMR time scale and minor and major compounds in both mixtures could not be distinguished.

A square-planar structure around the palladium is proposed for all four compounds in a similar way to **8** [2a]. Two coordination sites are occupied by the two carbene carbons to form a six-membered metallacycle with a boat conformation. The other two coordination sites are occupied by the halide atoms. Differences can be observed between the ^{1}H NMR signals of the 2-hydroxyethylene groups and the CH of the metallacyclic ring in the minor and major isomers. These differences are due to the fact that the 2-hydroxyethyl moieties are in axial positions in one compound (**6a** and **7a**) and equatorial positions in the other (**6b** and **7b**) and boat-to-boat inversions take place, as shown in Scheme 4. We propose that the major isomers have the 2-hydroxyethyl groups in axial positions (**6a** and **7a**) whereas they are in equatorial positions in the minor isomers (**6b** and **7b**) [19].

Our next goal was to the replace the hydroxyl groups with other units that may undergo nucleophilic substitu-

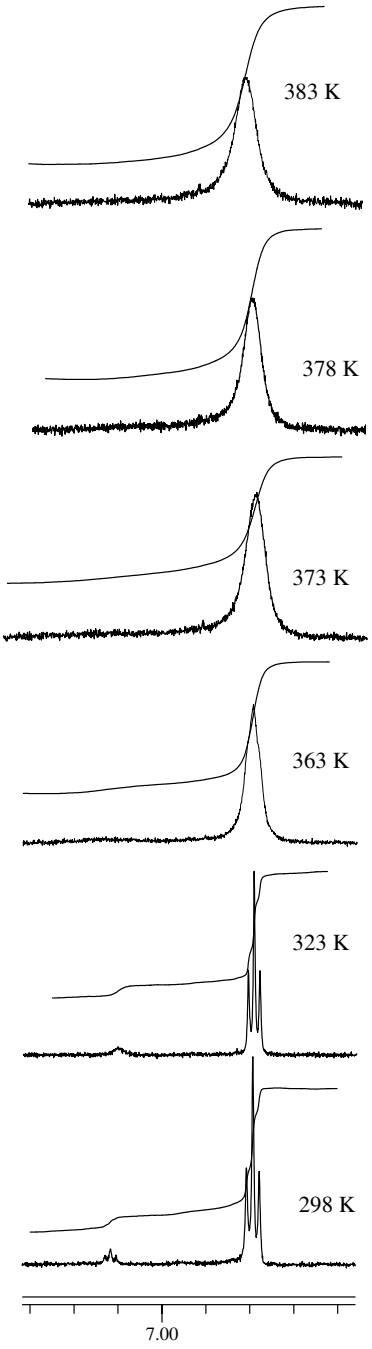


Fig. 3. Variable temperature ^{1}H NMR experiment of complex **6**.

tion; e.g., bromide or methanesulphonyl. Thus, the mixture of compound **6** was reacted with CBr_4 and triphenylphosphine in acetonitrile at room temperature and the corresponding bromide **9**, [Pd(L2)Br_2] was obtained (Scheme 5) as a new mixture of two isomers in an 8:1 ratio. These two components were found to be interchangeable at room temperature through a slow equilibrium on the NMR time scale, a situation confirmed by NOESY-1D experiments [17]. The two compounds have very similar ^{1}H NMR patterns, with the most important differences concerning the 2-bromoethyl moiety and, in particular, the triplets of the CH groups in the metallacyclic ring (as observed for **6**). Furthermore, the signals of the methylene groups are shifted to lower field in comparison to the corresponding signals of **6**, an observation that is consistent with the replacement of OH by Br.

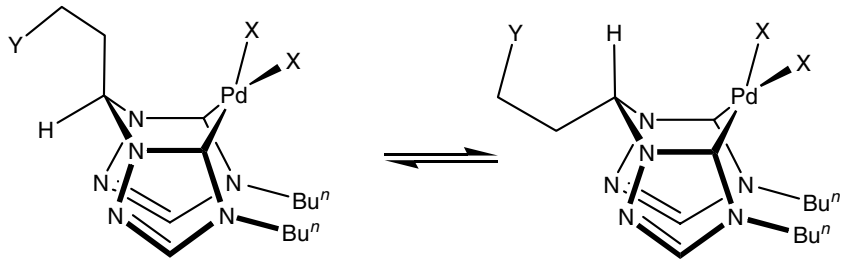
Similar to **6**, coalescence of the CH protons of the metallacyclic ring was observed at 105 °C. At higher temperature the two components of the mixture cannot be distinguished, a fact that indicates a fast equilibrium on the NMR time scale. However, it should be noted that partial decomposition (10–15%) was observed. New signals in the ^{1}H NMR spectrum of new unidentified products appeared.

As indicated for **6**, we propose that these two isomers of **9** have a square-planar structure around the palladium, with two coordination sites occupied by the two carbene carbons to form a six-membered metallacycle with a boat conformation. The other two coordination sites are occupied by the bromine atoms. The major compound has the 2-bromoethyl moiety in an axial position (**9a**) and the minor isomer has it in the equatorial position (**9b**) [19]. In addition, boat-to-boat inversions take place between these two compounds, as shown in Scheme 4.

Methanesulphonate derivative [Pd(L3)Br_2] (**10**) (Scheme 5) was obtained from the mixture **6** by reaction with methanesulphonyl chloride in the presence of triethylamine in CH_2Cl_2 at room temperature. A new mixture of isomers (8:1 ratio) was obtained and these components were interchangeable at room temperature through a slow equilibrium on the NMR time scale, a situation confirmed by NOESY-1D experiments [17]. The two compounds gave similar ^{1}H NMR spectra, with the most marked differences observed in the signals due to the methanesulphonyloxyethyl moiety, which is consistent with the presence of axial and equatorial isomers. Coalescence of the CH protons of the metallacyclic ring was again observed at 105 °C. At higher temperature the two isomers are not distinguishable because the equilibrium is fast on the NMR time scale. However, it should be noted that partial decomposition (25–30%) was observed. New signals in the ^{1}H NMR spectrum of new unidentified products appeared.

The aforementioned mixture of compounds **10** gives ^{1}H NMR patterns similar to that of **6** – except for the two singlets at 3.20 and 3.24 ppm, which were assigned to the methyl groups of the sulphonic ester of the major and minor compounds, respectively. The signals of the methylene groups bonded to oxygen atoms (4.11 and 4.71 ppm for major and minor, respectively) are shifted to lower field in comparison to the corresponding signals in hydroxycarbene **6** (3.54 and 3.90 ppm). This change is consistent with the formation of a sulphonate ester.

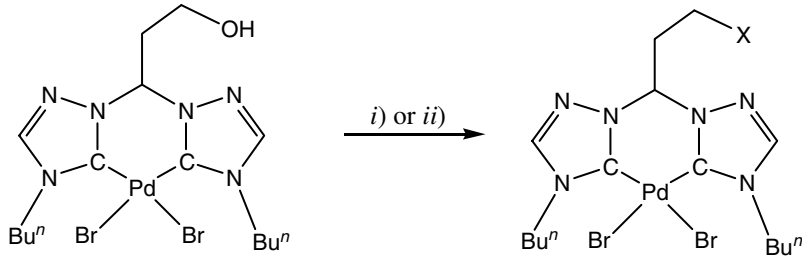
The structure proposed for the two isomers has a square-planar geometry around the palladium atom;



6a: X = Br, Y = OH
7a: X = I, Y = OH
9a: X = Br, Y = Br
10a: X = Br, Y = OMs

6b: X = Br, Y = OH
7b: X = I, Y = OH
9b: X = Br, Y = Br
10b: X = Br, Y = OMs

Scheme 4.



6

9: X = Br
10: X = OMs

Scheme 5. (i) CBr_4, PPh_3, CH_3CN, r.t. (ii) MsCl, Et_3N, CH_2Cl_2, r.t.

two coordination sites are occupied by the carbene carbons to give a six-membered metallacyclic ring with a boat conformation and the other two positions are occupied by the bromine atoms. The sulphonyloxyethyl groups are in axial positions for the major compound and equatorial positions for the minor component [19] – as indicated in Scheme 4. In addition, a boat-to-boat inversion takes place at room temperature between these two compounds.

The activation energies for this fluxional process in DMSO-d_6 were determined by examining the coalescence temperatures of the CH protons of the metallacyclic rings. The thermodynamic parameters are summarized in Table 1.

The absence of a boat-to-boat inversion at room temperature, which was reported by us for compound **8** [2a], warrants further comment. The activation energy of the inversion of **8** (78.12 kJ/mol) is lower than that observed for **7** (83.86 kJ/mol), meaning that **8** must be in a more rapid conformational equilibrium than **7** at room temperature. When a NOESY-1D experiment was performed on **8**, a signal was not observed in the negative phase other than that of the irradiated proton. This result is probably a consequence of the inversion rate not being high enough to observe formal magnetization transference from one conformer to the other.

Table 1
Activation parameters

Compound	T_c (K)	$\Delta G^{\#}$ (kJ/mol) [20]
6	378	74.75 ± 0.5
7	421	83.86 ± 0.6
9	378	75.01 ± 0.5
10	378	75.23 ± 0.3

3. Conclusions

Palladium–biscarbene complexes derived from an *N*,*N*′-bis(1,2,4-triazol-1-yl)methane that has an alkyl group functionalized with hydroxyl, methanesulphonate or bromide have been synthesized. Each product is obtained as a non-equimolecular mixture of conformers and these have a six-membered metallacyclic structure in a boat conformation. The substituent of the metallacycle is in an axial position for the major conformer and equatorial for the minor one.

4. Experimental

Solvents were purified by distillation from appropriate drying reagents before use. All reagents were used

as received and without further purification. When necessary, work was carried out using standard Schlenk techniques under an atmosphere of dry argon. Melting points were determined in capillary tubes on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyzer. Electron Impact (EI) (working at 70 V and 200 °C) experiments were performed on a VG Autospec instrument belonging to Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid. IR spectra were recorded on a Nicolet 550 spectrophotometer (FT-IR). NMR spectra were recorded in $CDCl_3$ on a Varian Inova-500 instrument with TMS or the solvent carbon signal as the standards, operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Chemical shifts are expressed in parts per million (δ). The signals were assigned with the help of NOESY-1D.

4.1. Synthesis of 1,1′-(3-hydroxypropylidene)bis(4-butyl-1H-1,2,4-triazolium) ditosylate (5)

A mixture of 1,1′-(3-hydroxypropylidene)bis(4-butyl-*H*-1,2,4-triazole) (**4**) (1.00 g, 5.15 mmol) and butyl tosylate (15 mL) was heated and stirred at 100 °C in a 25 mL round-bottomed flask for 24 h. The crude material was washed with ethyl acetate and the product was obtained as a colourless solid after crystallization from methanol/ethyl ether. Yield 99%; m.p. 187–191 °C. IR (KBr): 3368 (OH). Anal. found: C, 53.21; H, 6.38; N, 12.85%. Calc. for $C_{29}H_{42}N_6O_7S_2$: C, 53.52; H, 6.50; N, 12.91. ^1H NMR (DMSO-d_6): $\delta = 0.88$ (t, $J = 7.3$ Hz, 6H, $CH_2CH_2CH_2CH_3$); 1.28 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.79 (m, 4H, $NCH_2CH_2CH_2CH_3$), 2.28 [s, 6H, CH_3(Ts)], 2.81 (q, $J = 6.2$ Hz, 2H, $CHCH_2CH_2OH$), 3.50 (pseudo-t, $J = 5.5$ Hz, 2H, $CHCH_2CH_2OH$), 4.27 (t, $J = 7.5$ Hz, 4H, $CH_2CH_2CH_2CH_3$), 5.01 (bs, 1H, OH), 7.11 (d, $J = 8$ Hz, 4H, Ts) and 7.47 (d, $J = 8$ Hz, 4H, Ts), 7.59 (t, $J = 7.3$ Hz, 1H, $CHCH_2CH_2OH$), 9.43 [s, 2H, H3 (1,2,4-triazole)], 10.60 [s, 2H, H5 (1,2,4-triazole)]. ^{13}C NMR (DMSO-d_6): $\delta = 13.2$, 18.7, 20.8, 30.6, 33.4, 47.7, 55.3, 71.7, 125.4, 128.1, 137.7, 144.6, 145.3, 145.5.

4.2. Synthesis of 1,1′-(3-hydroxypropylidene)bis(4-butyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)palladium(II) dibromide (6)

Compound **5** (150 mg, 0.23 mmol), DMSO (2 mL), KBr (83.30 mg, 0.7 mmol) and Pd $(OAc)_2$ (46.42 mg, 0.207 mmol) were added, in that order, to THF (100 mL) in a 500 mL two-necked round-bottomed flask. The resulting brown suspension was stirred for 1 h. The THF was evaporated under vacuum at 20 mmHg and the DMSO was distilled at 10^{-3} mmHg. The residue was washed with toluene (3×50 mL) and the product was extracted with THF (3×80 mL). The THF was evaporated and the product was purified by column chromatography (silica gel, CH_2Cl_2/acetone 10:1) to give an oil, which crystallized when washed with diethyl ether under ultrasound. The pure product was obtained by crystallization from CH_2Cl_2/diethyl ether. Yield 60%; m.p.: 144–146 °C. MS-FAB$^+$: $m/z = 492.8$ $[M\text{-}Br]^+$, 1064.5 $[2M\text{-}Br]^+$. IR (KBr): 3405 (OH). Anal. found: C, 31.71; H, 4.63; N, 14.82%. Calc. for $C_{15}H_{26}Br_2N_6OPd$: C, 31.46; H, 4.58; N, 14.68. Compound **6a**, ^1H NMR (DMSO-d_6): $\delta = 0.88$ (t, $J = 7.4$ Hz, 6H, CH_3), 1.18–1.25 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.73–2.88 (m, 4H, $CH_2CH_2CH_2CH_3$), 3.04 (q, $J = 6.1$ Hz, 2H, $CHCH_2CH_2OH$), 3.54 (q, $J = 5.4$ Hz, 2H, $CHCH_2CH_2OH$), 4.14–4.19 (m, 2H, one H for each $CH_2CH_2CH_2CH_3$), 4.84–4.98 (bs, 2H, one H for each $CH_2CH_2CH_2CH_3$), 5.05 (t, $J = 4.8$ Hz, 1H, OH), 6.79 (t, $J = 7.3$ Hz, 1H, $CHCH_2CH_2OH$), 8.92 [s, 2H, H3 (1,2,4-triazole)]. ^{13}C NMR ($CDC1_3$): $\delta = 13.6$, 19.6, 32.9, 41.7, 49.9, 57.2, 77.10, 143.0, 163.8. Compound **6b**, ^1H NMR (DMSO-d_6): $\delta = 2.84$ (q, $J = 6.7$ Hz, 2H, $CHCH_2CH_2OH$), 3.90 (q, $J = 5$ Hz, 2H, $CHCH_2CH_2OH$), 4.78–4.90 (bs, 2H, one H for each $CH_2CH_2CH_2CH_3$), 5.08 (t, $J = 5.5$ Hz, 1H, OH), 7.12 (t, $J = 6.3$ Hz, 1H, $CHCH_2CH_2OH$), 8.88 [s, 2H, H3 (1,2,4-triazole)].

4.3. Synthesis of 1,1′-(3-hydroxypropylidene)bis(4-butyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)palladium(II) diiodide (7)

Compound **5** (150 mg, 0.23 mmol), KI (76.53 mg, 0.46 mmol) and $Pd(OAc)_2$ (46.42 mg, 0.21 mmol) were added, in that order, to THF (100 mL) in a 500 mL two-necked round-bottomed flask. The resulting brown suspension was stirred at 0 °C for 24 h. The crude mixture was filtered and the solvent evaporated under vacuum. The residue was purified by column chromatography (silica gel, acetone/CH_2Cl_2 1:20). The pure product was obtained as a red solid after crystallization from CH_2Cl_2/diethyl ether. Yield 85%; m.p. 200–203 °C. MS-FAB$^+$: $m/z = 538.9$ $[M\text{-}I]^+$, 1205.1 $[2M\text{-}I]^+$. IR (KBr): 3402 (OH). Anal. found: C, 26.68; H, 3.65; N, 12.41%. Calc. for $C_{15}H_{26}I_2N_6OPd$: C, 27.03; H, 3.93; N, 12.61. Compoud **7a**, ^1H-NMR (DMSO-d_6): $\delta =$ 0.88 (t, $J = 7.3$ Hz, 6H, CH_3), 1.17–1.25 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.71–1.88 (m, 4H, $CH_2CH_2CH_2CH_3$), 3.11 (q, $J = 6.1$ Hz, 2H, $CHCH_2CH_2OH$), 3.53 (pseudo-q, $J = 4.5$ Hz, 2H, $CHCH_2CH_2OH$), 4.15–4.20 (m, 2H, one H for each $CH_2CH_2CH_2CH_3$), 4.74–4.90 (bs, 2H, one H for each $CH_2CH_2CH_2CH_3$), 5.05 (pseudo-t, $J = 4.5$, 1H, OH), 6.82 (t, $J = 7.5$ Hz, 1H, $CHCH_2CH_2OH$), 8.93 [s, 2H, H3 (1,2,4-triazole)]. ^{13}C NMR ($CDCl_3$): $\delta = 13.6$, 19.5, 32.6, 40.8, 50.8, 57.3, 77.6, 142.7, 167.9. Compound **7b**, ^1H-NMR (DMSO-d_6): $\delta = 2.86$ (q, $J = 6.7$ Hz, 2H, $CHCH_2CH_2OH$), 3.90 (q, $J = 6.7$ Hz, 2H, $CHCH_2CH_2OH$), 4.69–4.80 (bs, 2H,

one H for each $CH_2CH_2CH_2CH_3$), 5.11 (t, $J = 7.5$ Hz, 1H OH), 7.12 (t, $J = 6.3$ Hz, 1H, $CHCH_2CH_2OH$), 8.90 [s, 2H, H3 (1,2,4-triazole)].

4.4. Synthesis of 1,1'-(3-bromopropylidene)bis(4-butyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)palladium(II) dibromide (**9**)

To a solution of **6** (100 mg, 0.17 mmol) and carbon tetrabromide (230 mg, 0.69 mmol) in acetonitrile (10 mL) at 0 °C was added a solution of triphenylphosphine (182 mg, 0.69 mmol) in acetonitrile (10 mL). The reaction mixture was stirred under argon for 14 h at room temperature. Potassium carbonate was added and the stirring was maintained until the organic layer had been neutralized. The crude mixture was filtered and the solvent evaporated under vacuum. The residue was purified by column chromatography (silica gel, CH_2Cl_2/acetone, 16:1) followed by crystallization from CH_2Cl_2/Et_2O. Yield 92%; m.p. 202–204 °C. MS-FAB$^+$: $m/z = 554.8$ $[M\text{-}Br]^+$, 1190.5 $[2M\text{-}Br]^+$. Anal. found: C, 28.40; H, 4.04; N, 13.09%. Calc. for $C_{15}H_{25}Br_3N_6Pd$: C, 28.35; H, 3.96; N, 13.22. Compound **9a**, ^{1}H NMR (DMSO-d_6): $\delta = 0.88$ (t, $J = 7.3$ Hz, 6H, CH_3), 1.19–1.26 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.73–1.88 (m, 4H, CH_2CH_2-CH_2CH_3), 3.46 (q, $J = 6.7$ Hz, 2H, $CHCH_2CH_2Br$), 3.64 (t, $J = 6.5$ Hz, 2H, $CHCH_2CH_2Br$), 4.14–4.20 (m, 2H, one H for each $CH_2CH_2CH_2CH_3$), 4.88–4.95 (m, 2H, one H for each $CH_2CH_2CH_2CH_3$), 6.88 (t, $J = 7.3$ Hz, 1H, $CHCH_2CH_2Br$), 8.94 [s, 2H, H3 (1,2,4-triazole)]. ^{13}C NMR ($CDCl_3$): $\delta = 13.6$, 19.6, 26.3, 32.9, 41.9, 49.9, 77.6, 143.3, 164.2. Compound **9b**, ^{1}H NMR (DMSO-d_6): $\delta = 3.21$ (q, $J = 7.2$ Hz, 2H, $CHCH_2$-CH_2Br), 3.95 (t, 7.8 Hz, 2H, $CHCH_2CH_2Br$), 4.79–4.89 (bs, 2H one H for each $CH_2CH_2CH_2CH_3$), 7.17 (t, $J = 6.3$ Hz, 1H, $CHCH_2CH_2Br$), 8.91 [s, 2H, H3 (1,2,4-triazole)].

4.5. Synthesis of 1,1'-(3-methanesulphonyloxypropylidene)bis(4-butyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)palladium(II) dibromide (**10**)

A stirred mixture of **6** (100 mg, 0.17 mmol) and freshly distilled Et_3N (36 μL, 0.26 mmol) in CH_2Cl_2 was cooled to 0 °C and treated dropwise with a solution of methanesulphonyl chloride (20 μL, 0.26 mmol) in CH_2Cl_2 (10 mL). The mixture was allowed to warm up to room temperature over a further 2 h. $Et_3N \cdot HCl$ was then removed by centrifugation and the solvent evaporated under vacuum. Compound **10** was obtained as a yellow oil and this was purified by column chromatography (silica gel, CH_2Cl_2/acetone, 16:1) followed by crystallization from CH_2Cl_2/Et_2O. Yield 90%; m.p. 188–191 °C. MS-FAB$^+$: $m/z = 570.8[M\text{-}Br]^+$, 1222.7 $[2M\text{-}Br]^+$. Anal. found: C, 29.60; H, 4.49; N, 12.72%. Calc. for $C_{15}H_{28}Br_2N_6O_3PdS$: C, 29.53; H, 4.34; N, 12.91. Compound **10a**, ^{1}H NMR (DMSO-d_6): $\delta = 0.88$ (t,$J = 7.3$ Hz, 6H, $CH_2CH_2CH_2CH_3$), 1.19–1.26 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.75–1.87 (m, 4H, CH_2CH_2-CH_2CH_3), 3.20 (s, 3H, CH_3SO_3), 3.33–3.38 (m, 2H, $CHCH_2CH_2O$), 4.15–4.21 (m, 2H, one H for each $CH_2CH_2CH_2CH_3$), 4.11 (t, $J = 5.5$ Hz, 2H, $CHCH_2$-CH_2O), 4.85–4.98 (m, 2H, one H for each $CH_2CH_2CH_2$-CH_3), 6.95 (t, $J = 7.3$ Hz, 1H, $CHCH_2CH_2O$), 8.93 [s, 2H, H3 (1,2,4-triazole)]. ^{13}C NMR ($CDCl_3$): $\delta = 13.6$, 19.6, 32.9, 37.8, 38.6, 49.9, 64.1, 76.1, 143.5, 164.0. Compound **10b**, ^{1}H NMR (DMSO-d_6): $\delta = 3.11-3.15$ (m 2H, $CHCH_2CH_2O$), 3.24 (s, 3H, CH_3SO_3), 4.71 (t, $J = 6.8$ Hz, 2H, $CHCH_2CH_2O$), 4.80–4.90 (bs, 2H, one H for each $CH_2CH_2CH_2CH_3$), 7.23 (t, $J = 5.5$ Hz, 1H, $CHCH_2CH_2O$), 8.91 [s, 2H, H3 (1,2,4-triazole)].

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References

[1] (a) D. Bourissou, O. Guerret, F. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39;
(b) A.J. Arduengo III, Acc. Chem. Res. 32 (1999) 913;
(c) W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290;
(d) W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162;
(e) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(f) C.D. Frohning, C.W. Kolhpainter, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallics Compounds, vol. 1, VCH, Weinheim, 1996;
(g) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C.W. Lehmann, R. Mynott, F. Stelzer, O.R. Thiel, Chem. Eur. J. 7 (2001) 3236;
(h) H.M.J. Wang, C.S. Vasam, T.Y.R. Tsai, S.-H. Chen, A.H.H. Chang, I.J.B. Lin, Organometallics 24 (2005) 486;
(i) E. Peris, R. Crabtree, Coord. Chem. Rev. 248 (2004) 2239;
(j) N. Kuhn, A. Al-Sheikh, Coord. Chem. Rev. 249 (2005) 829;
(k) W.A. Herrmann, K. Öfele, D.v. Preysing, S.K. Schneider, J. Organomet. Chem. 687 (2003) 229;
(l) X. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 126 (2004) 13464;
(m) L.P. Spencer, S. Winston, M.D. Fryzuk, Organometallics 23 (2004) 3372;
(n) P. de Frémont, N. Scout, E.D. Stevens, S.P. Nolan, Organometallics 24 (2005) 2411;
(o) J.W. Sprengers, J. Wassenaar, N.D. Clement, K.J. Cavell, C.J. Elsevier, Angew. Chem. Int. Ed. 44 (2005) 2026;
(p) J.A. Loch, M. Albrecht, E. Peris, J. Mata, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 700;
(q) N.D. Clement, K.J. Cavell, C. Jones, C.J. Elsevier, Angew. Chem. Int. Ed. 43 (2004) 1277;
(r) N.M. Scott, R. Dorta, E.D. Stevens, A. Correa, L. Cavallo, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 3516.
[2] (a) G. Bertrand, E. Díez-Barra, J. Fernández-Baeza, H. Gornitzka, A. Moreno, A. Otero, R.I. Rodríguez-Curiel, J. Tejeda, Eur. J. Inorg. Chem. (1999) 1965;

(b) O. Guerret, S. Solé, H. Gornitzka, G. Trinkier, G. Bertrand, J. Organomet. Chem. 600 (2000) 112;
(c) C. Buron, L. Stelzig, O. Guerret, H. Gornitzka, V. Romanenko, G. Bertrand, J. Organomet. Chem. 664 (2002) 70;
(d) K. Meils, D. De Vos, P. Jacobs, F. Verpoort, J. Organomet. Chem. 671 (2003) 131;
(e) K. Melis, P. Samulkiewicz, J. Rynkowski, F. Verpoort, Tetrahedron Lett. 43 (2002) 2713;
(f) H. Braband, U. Abram, Chem. Commun. (2003) 2436;
(g) D. Enders, K. Breuer, U. Kallfass, T. Balensiefer, Synthesis (2003) 1292;
(h) T.M. Trnka, J.P. Morgan, M.S. Sanford, T.E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M.W. Day, R.H. Grubbs, J. Am. Chem Soc. 125 (2003) 2546.

[3] (a) M. Poyatos, F. Márquez, E. Peris, C. Claver, E. Fernández, New J. Chem. (2003) 425;
(b) E. Mas-Marzá, A.M. Segarra, C. Claver, E. Peris, E. Fernández, Tetrahedron Lett. 44 (2003) 6595.

[4] M. Mayr, B. Mayr, M.R. Buchmeiser, Angew. Chem. Int. Ed. 40 (2001) 3839.

[5] M. Mayr, M.R. Buchmeiser, K. Wurst, Adv. Synth. Catal. 344 (2002) 712.

[6] S. Prühs, C.W. Lehmann, A. Fürstner, Organometallics 23 (2004) 280.

[7] M.T. Zarka, M. Bortenschlager, K. Wurs, O. Nuyken, R. Weberskirch, Organometallics 23 (2004) 4817.

[8] D. Enders, H. Gielen, J. Organomet. Chem. 617–618 (2001) 70.

[9] W.A. Herrmann, L.J. Gooßen, M. Spiegler, J. Organomet. Chem. 547 (1997) 357.

[10] (a) K. Grela, M. Tryznowski, M. Bieniek, Tetrahedron Lett. 43 (2002) 9055;
(b) Q. Yao, A. Rodríguez Mota, Tetrahedron Lett. 45 (2004) 2447;
(c) S.J. Connon, A.M. Dunne, S. Blechert, Angew. Chem. Int. Ed. 41 (2002) 3835;
(d) S.B. Garber, J.S. Kingsbyry, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168.

[11] J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Hermann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. (2000) 1773.

[12] E. Díez-Barra, J. Guerra, R.I. Rodríguez-Curiel, S. Merino, J. Tejeda, J. Organomet. Chem. 660 (2002) 50.

[13] E. Díez-Barra, A. de la Hoz, R.I. Rodríguez-Curiel, J. Tejeda, Tetrahedron 53 (1997) 2253.

[14] (a) P.L. Arnold, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2001) 2340;
(b) P.L. Arnold, A.C. Scarisbrick, Organometallics 23 (2004) 2519.

[15] E. Díez-Barra, J. Guerra, V. Homillos, S. Merino, J. Tejeda, Tetrahedron Lett. 45 (2004) 6937.

[16] E. Díez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, J. Tolosa, Arkivoc (2005) 159.

[17] When signals of the minor compounds were irradiated, the NOESY-1D spectra show signals with a negative phase for the protons of the same groups of the major compounds, and enhancement of the signals of the minor and major compounds are observed. These facts indicate that there is an interchange between minor and major components and the interchange times are greater than the relaxation times. Formal magnetization transferences from the minor to the major compounds did occur.

[18] G. Szalontai, G. Besenyei, Inorg. Chim. Acta 375 (2004) 4413.

[19] As observed by Jalón [19a,b] and ourselves [19c] in similar metallacycles, the steric repulsion of the equatorial substituent with the N2 of the heterocycles is thought to be responsible for the lower stability of the equatorial derivatives: (a) N. Arroyo, F. Gómez-de la Torre, F.A. Jalón, B.R. Manzano, B. Moreno-Lara, A.M. Rodríguez, J. Organomet. Chem. 603 (2000) 174;
(b) M.C. Carrión, A. Díaz, A. Guerrero, F. Jalón, B.R. Manzano, A. Rodríguez, New J. Chem. 26 (2002) 305;
(c) E. Díez-Barra, J. Guerra, I. López-Solera, S. Merino, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, Organometallics 22 (2003) 541.

[20] R.J. Abraham, J. Fisher, P. Loftus, Introduction to NMR Spectroscopy, Wiley, New York, 1988, p. 196 (reprinted in July 1990).