Synthesis, Characterization and Dynamic Behavior of Mono- and Dinuclear Palladium(II) Carbene Complexes Derived From 1,1′-Methylenebis(4-alkyl-1,2,4-triazolium) Diiodides

Guy Bertrand,[b] Enrique Díez-Barra,*[a] Juan Fernández-Baeza,[a] Heinz Gornitzka,[b] Andrés Moreno,[a] Antonio Otero,[a] René Ignacio Rodríguez-Curiel,[c,d] and Juan Tejeda[a]

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Mononuclear palladium carbene complexes **2a–c** and **3** derived from 1,1′-methylenebis(4-alkyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) have been obtained by the reaction of 1,1′-methylenebis(4-alkyl-1,2,4-triazolium) diiodides **1a–d** with palladium acetate under mild conditions. The mononuclear complexes **2a–c** have been transformed into their corresponding *trans*-binuclear complexes **4a–c**. All compounds were characterized by spectroscopic techniques and the dynamic behavior of **2a–c** and **4a–c** has been studied. The X-ray structures of **2a** and **4c** are reported.

Introduction

A large number of palladium(II) complexes with bidentate ligands (L−L) are known, with this kind of ligand acting predominantly as a chelate to form mononuclear *cis*-[PdX_2(L−L)] complexes. Although some examples of chelate complexes with a *trans*-configuration are known, they are rare; normally, bidentate ligands act as bridges when they form palladium(II) complexes with a *trans*-configuration, but there are relatively few examples of *trans*-binuclear palladium(II) complexes (*trans*-[PdX_2(μ-L−L)]$_2$).[1,2]

In recent years, heterocyclic carbenes have generated a great deal of interest and a large number of reports covering theoretical aspects,[3] synthetic approaches,[4] coordination[4b,4c,4e,5] and catalytic[5g,5k,6] applications have been published. Imidazole and imidazoline rings with different substitution patterns have been extensively studied, several free carbenes and a great number of complexes derived from 2,3-dihydro-1*H*-imidazole-2-ylidene have been obtained.[4] However, carbenes based on the 1,2,4-triazole ring, where an additional nitrogen atom is present in the ring, have received little attention. As far as we know 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene is the only example of a free carbene isolated.[7] Several rhodium,[6c,6e] and *cis*- and *trans*-palladium[8] complexes derived from 4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene have been prepared, a tungsten compound, with a similar structure to the chelate carbene complex, derived from 1,1′-methylenebis(4-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)[9] and 1,1′-methylenebis(4-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)-1,1′-methylenebis(3-methyl-4,5-dihydro-1*H*-imidazole-5-ylidene)palladium(II) diiodide[5q] have also been reported.

In this paper we report the preparation of mononuclear palladium(II) complexes derived from 1,1′-methylenebis(4-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) (mbmdty), 1,1′-methylenebis(4-isopropyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) (mbidty), 1,1′-methylenebis(4-butyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) (mbbdty) and 1,1′-methylenebis(4-octyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) (mbodty), and their transformation into the corresponding *trans*-binuclear complexes.

Results and Discussion

Synthesis of [PdI_2(mbidty)] (2a), [PdI_2(mbbdty)] (2b) and [PdI_2(mbodty)] (2c)

Carbene complexes were prepared by a modification of the palladium(II) acetate route reported by Herrmann for the synthesis of similar compounds.[5g,6a] The reaction of the 1,1′-methylenebis(4-alkyl-1,2,4-triazolium) diiodides[10] (**1a−c**) with palladium(II) acetate in THF at 0°C led exclusively to the mononuclear species **2a−c**, as outlined in Scheme 1. The acidity of the H5 protons of the 1,2,4-triazole ring is higher than that of the H2 imidazole protons. This fact permits very mild reaction conditions in comparison with the usual procedures described for the synthesis of imidazole carbene complexes.[5g,6a]

Compounds **2a−c** present the same patterns in the ^{1}H- and ^{13}C{^{1}H} NMR spectra in [D_6]DMSO, except for the signals of the alkyl substituents. At room temperature an

[a] Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Química,
Universidad de Castilla-La Mancha, Campus Universitario, 13071-Ciudad Real, Spain
Fax: (internat.) + 34-926/295318
E-mail: ediez@qino-cr.uclm.es
[b] Laboratoire Hétérochimie Fondamentale et Appliquée, Bat. 2R1,
Université Paul Sabatier, 118, Route de Narbonne, 31062-Toulouse Cedex, France
Fax: (internat.) + 33-561/558204
[c] Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Química,
Universidad de Castilla-La Mancha, Campus Universitario, 13071-Ciudad Real, Spain
Fax: (internat.) + 34-926/295318
[d] Laboratorio de Síntesis Orgánica. Facultad de Química, Universidad de La Habana,
Zapata e/ Mazón y G, 10400-Ciudad de La Habana, Cuba
Fax: (internat.) + 537/333502

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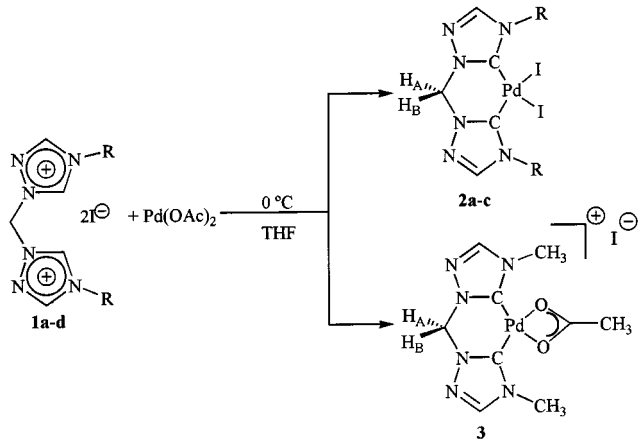


Scheme 1. Summary of reactions leading to the preparation of **2a**−**c** and **3**

AB system was observed for the two methylene bridge protons (H_A and H_B) at about 6.53 and 6.95 ppm. Their coupling constants are in agreement with a geminal coupling. This assignment has been confirmed by NOE difference and HETCOR experiments; NOE intensities of 26% (**2a**), 13% (**2b**), and 14% (**2c**) between the methylene bridge protons have been observed and, in addition, HETCOR experiments show a correlation between each of the signals of the AB system in the ^{1}H NMR spectrum with only one signal in the $^{13}C\{^1H\}$ NMR spectrum (δ = 66.6, 66.7 and 66.7, respectively).

Each compound (**2a**−**c**) showed only one set of signals in the ^{1}H- and $^{13}C\{^1H\}$ NMR spectra for the alkyl substituents (the assignment was confirmed by HETCOR and NOE experiments).[12] These results indicate the equivalence of the alkyl groups, which is in agreement with a symmetric structure. However, in the ^{1}H NMR spectra two doublets of triplets were observed for **2b** and **2c** − one for each proton of N4−CH_2 (δ = 4.18 and 4.80 for **2b** and δ = 4.18 and 4.78 for **2c**) − due to a vicinal coupling (J = 7.1 Hz for both compounds) and a geminal coupling (J = 13.4 Hz for **2b** and 13.6 Hz for **2c**), which show the nonequivalence of the these two protons. In the ^{1}H NMR spectrum the isopropyl groups (**2a**) showed two doublets (δ = 1.33 and 1.53) for the CH_3 protons, which indicates that the methyl groups are nonequivalent, although these nonequivalent methyl groups are from the same isopropyl group because only one signal (δ = 5.41, sep) was observed for N4−CH, which indicates that the two isopropyl groups are equivalent. The equivalence of the isopropyl groups and the nonequivalence of the methyl groups was confirmed by $^{13}C\{^1H\}$ NMR spectroscopy, in which only one signal for N4−CH (δ = 52.7) and two signals for CH_3 (δ = 21.0 and 23.4) were observed.

The patterns in the ^{1}H- and $^{13}C\{^1H\}$ NMR spectra for compounds **2a**−**c** indicate that the two triazole rings are equivalent. We observed only one signal at lower field for H3 in the ^{1}H NMR spectrum (δ = 9.12, **2a**; 8.92, **2b**; 8.90, **2c**), which integrated for two protons, one for each heterocycle. In the $^{13}C\{^1H\}$ NMR spectra of all three compounds two signals appeared at lower field, one for C3 at 142.3 ppm (**2a**), 144.7 ppm (**2b**) or 144.8 ppm (**2c**) and the other for C5 at 166.7 ppm (**2a**), 166.3 ppm (**2b**) or 166.3 ppm (**2c**). The chemical shifts of C5 are in agreement with a coordinated heterocyclic carbenic carbon.[8b] This assignment has also been confirmed by HETCOR experiments.

The NMR spectroscopic and microanalytical data are in accordance with a 1,1′-methylenebis(4-alkyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) system, although it is not possible to distinguish between mononuclear or binuclear palladium(II) complexes. The FAB-MS for compounds **2a**−**c** showed a peak at an *m*/*z* value double that expected for the mononuclear complexes. Nevertheless, by CI-MS with direct sample introduction the appropriate molecular peak for the mononuclear species was observed. This behavior may be explained by the formation of dimmeric species in solution, a phenomenon that has been observed previously in other systems.[11]

On the basis of the spectroscopic data a square-planar structure for palladium is proposed. Two coordination sites are occupied by two carbenes forming a rigid six-membered metallacyclic structure with a boat-conformation, and the other two coordination sites are occupied by the two iodine atoms (Figure 1). In our complexes the alkyl groups probably create sufficient steric hindrance to prevent boat-to-boat inversion.

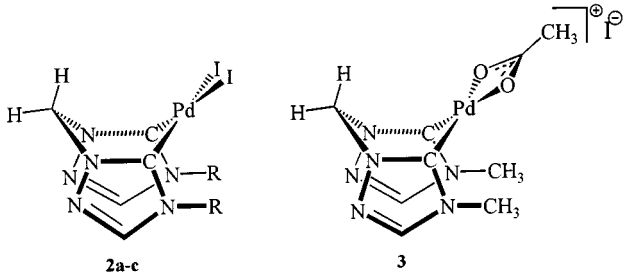


Figure 1. Proposed structures for **2a**−**c** and **3**

In order to confirm this proposal an X-ray crystal structure determination for **2a** was carried out. The solid state structure of this compound is shown in Figure 2. Compound **2a** is mononuclear in the solid state. The coordination sphere of the palladium atom shows a square planar geometry with the two iodide atoms in *cis*-positions.

Synthesis of [Pd(OAc)(mbmdty)]I (3)

Reaction of 1,1′-methylenebis(4-methyl-1,2,4-triazolium) diiodide[12] (**1d**) with palladium(II) acetate under the same conditions as for compounds **2a**−**c** (THF, 0°C) yielded an unexpected carbenic species, **3**, as shown in Scheme 1. This cationic palladium(II) dicarbene complex was characterized by IR, ^{1}H- and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry. The IR spectrum showed characteristic bands at 1408 and 1540 cm^{-1}, which correspond to $\nu_s(CO_2^-)$ and $\nu_a(CO_2^-)$, respectively. The ^{1}H NMR signals for the two

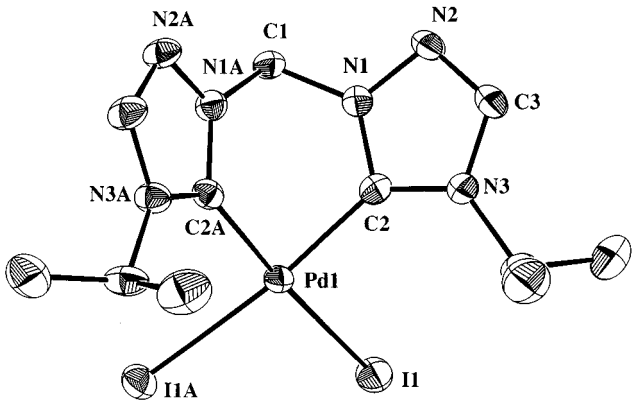


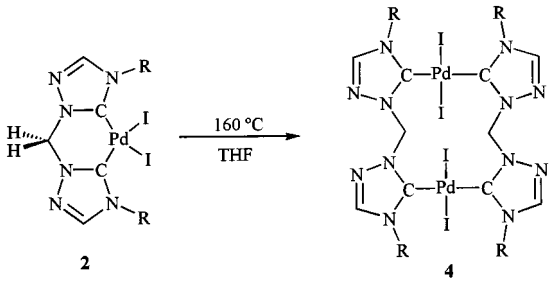
Figure 2. Solid state structure of **2a**; hydrogen atoms and a non-coordinated THF molecule are omitted for clarity; selected bond lengths [pm] and angles [°]: Pd1−C2 1.996(4), Pd1−I1 2.634(1); C2−Pd1−C2A 84.3(2), I1−Pd1−I1A 90.7(1), C2−Pd1−I1 92.2(1), C2−Pd1−I1A 173.2(1).

protons of the methylene bridge form an AB system with signals at 6.94 and 7.56 ppm, with a geminal coupling constant of 14.6 Hz. Moreover, H3 appears as a singlet at 8.95 ppm and we observed two other high-field singlets: one at 3.89 ppm for N4−CH_3 and the other at 1.87 ppm for the methyl group of the acetate. The $^{13}C\{^1H\}$ NMR spectrum showed three signals at lower field: 147.0, 152.0 and 181.7 ppm for C3, the carbenic carbon and COO, respectively. The carbon of the methylene bridge was observed as one signal at 65.0 ppm and two signals appeared at higher field: one at 23.6 ppm for the methyl of the acetate group and the other at 35.8 ppm for N4−CH_3.

CI-MS with direct sample introduction and FAB-MS of compound **3** showed mass peaks corresponding to the mononuclear complex (*m*/*z*: 343 D, $[M - I]^+$; 411 D, $[M - OAc]^+$) but with very low intensity. However, electrospray-MS showed these peaks with intensity of 100% and 66%, respectively. In a similar way to complexes **2a**−**c**, all spectroscopic data obtained for **3** are consistent with a rigid six-membered metallacyclic structure in the boat conformation, as shown in Figure 1.

Synthesis of $[PdI_2(\mu\text{-mbidty})]_2$ (4a), $[PdI_2(\mu\text{-mbbdty})]_2$ (4b) and $[PdI_2(\mu\text{-mbodty})]_2$ (4c)

Heating the carbene complexes **2a**−**c** in THF at 160°C in a Fisher−Porter bottle gave the new *trans*-binuclear palladium(II) species **4a**−**c** as the only products (Scheme 2). Compounds **4** show similar patterns in the ^1H- and $^{13}C\{^1H\}$ NMR spectra ([D_6]DMSO), except for the typical signals of the alkyl substituents. The NMR spectra of **4** were found to be different to those of the mononuclear complexes **2**: The ^1H NMR spectrum shows a very broad singlet at about 7.10 ppm (**4a**), 7.30 ppm (**4b** and **4c**) for the methylene bridges, a broad singlet due to N4−CH_2 for **4b** (δ = 4.40−4.60) and **4c** (δ = 4.30−4.50), and only one doublet (δ = 1.55) for all the methyl groups of the isopropyl units (**4a**). These facts indicate that the structure of the binuclear complexes **4a**−**c** is nonrigid and symmetrical at room temperature. This assignment is in agreement with the $^{13}C\{^1H\}$ NMR spectra, with one signal for the methylene bridges at δ = 67.0 (**4a**); 67.2 (**4b**); 67.3 (**4c**), one signal for N4−CH_2 (δ = 48.8, **4b**; 49.1, **4c**) and one signal for the CH_3 of the isopropyl groups (δ = 25.1, **4a**). The other signals in the ^1H- and $^{13}C\{^1H\}$ NMR spectra are typical for alkyl substituents.[12] In the ^1H NMR spectra only one signal appeared at low field (δ = 9.26, 9.03 and 9.02 for **4a**−**c**, respectively) for H3 of the heterocyclic rings, and these were correlated with only one signal in the $^{13}C\{^1H\}$ NMR spectra (δ = 143.5, **4a**; 145.7, **4b**; 145.8, **4c**). In the $^{13}C\{^1H\}$ NMR spectra we observed one signal of low intensity at lower field, corresponding to the carbenic carbon C5 (δ = 172.0, **4a**; 171.3, **4b**; 171.5, **4c**). This evidence corroborates the symmetrical structure indicated above.



a: R = Isopropyl, **b**: R = Butyl, **c**: R = Octyl

Scheme 2. Summary of reactions leading to the preparation of **4a**−**c**

In a similar way to compounds **2a**−**c**, both the spectroscopic and microanalytical data are in agreement with the structure of the 1,1′-methylenebis(4-alkyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene) system. However, these compounds could have either a mono- or binuclear structure. CI-MS with direct sample introduction, and FAB-MS, for compounds **4a**−**c** showed, without doubt, peaks corresponding to binuclear compounds.[12]

In order to ascertain whether the complexes exist in the *cis*- or *trans*-configuration in the solid state an X-ray crystal structure determination for **4c** was carried out. The solid state structure (Figure 3) shows a binuclear structure in which two dicarbene ligands act as a bridge between two palladium atoms with a *trans*-square planar geometry about the metal centers.

When the mononuclear compounds were transformed into the binuclear complexes a change in their configuration was observed; while the former showed a *cis*-configuration the latter presented a *trans*-configuration. This is reminiscent of the *cis*/*trans* isomerization observed by Herrmann for diiodobis(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)-palladium(II),[8b] in which the rearrangement took place without dissociation of the ligand. However, our results are not consistent with this model because it is not possible to prepare *trans*-chelate complexes with our biscarbenes. − they should act as bridges to form complexes with a *trans*-configuration and, therefore, dissociation of the ligand is necessary.

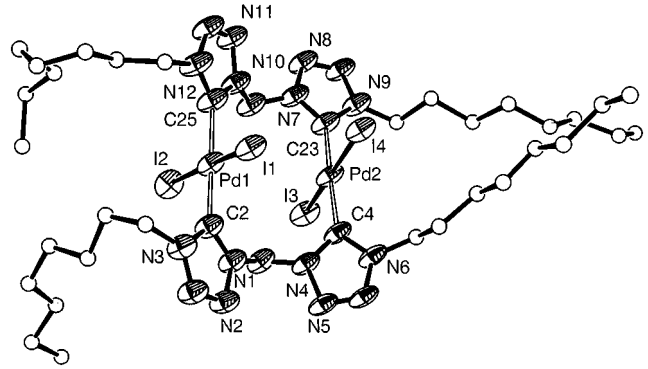
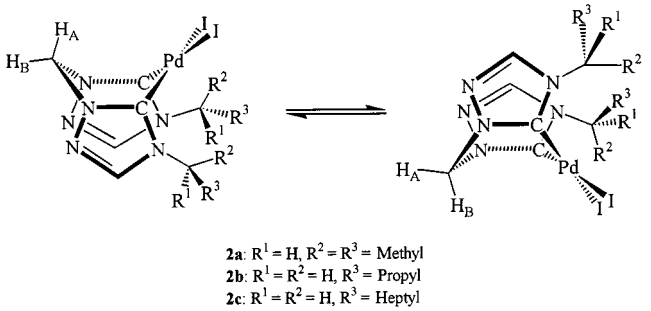


Figure 3. Solid state structure of **4c**; for clarity, the hydrogen atoms and a toluene molecule are omitted, and the octyl substituents are presented in a ball and stick style; selected bond lengths [pm] and angles [°]: Pd1−C2 1.970(17), Pd1−C25 2.018(17), Pd1−I1 2.619(2), Pd1−I2 2.600(2), Pd2−C4 2.017(16), Pd2−C23 1.973(16), Pd2−I3 2.595(2), Pd2−I4 2.599(2); C2−Pd1−C25 177.3(8), I1−Pd1−I2 174.2(1), C2−Pd1−I2 90.0(7), C25−Pd1−I2 92.2(7), C2−Pd1−I1 85.5(7), C25−Pd1−I1 92.3(7), C4−Pd2−C23 176.4(8), I3−Pd2−I4 173.9(1), C23−Pd2−I3 87.5(7), C4−Pd2−I3 90.9(6), C23−Pd2−I4 87.3(7), C4−Pd2−I4 94.1(6)



Scheme 3. Boat-to-boat inversion of **2a**−**c**

Study of the Dynamic Behavior of the Mononuclear and Binuclear Complexes

We have mentioned above that the structures of the mononuclear complexes **2a**−**c** are rigid at room temperature. However, when solutions of these compounds were heated some dynamic behavior was observed. The signals in the ^{1}H NMR spectra of the methylene bridge, N4-methylene for **2b** and **2c,** and methyl (isopropyl) groups for **2a** were observed during the dynamic study. When the ^{1}H NMR spectra of **2a**−**c** were recorded at high temperature, the AB systems corresponding to the diastereotopic protons of the methylene bridges coalesce. This indicates that boat-to-boat inversion takes place at high temperature as shown in Scheme 3.

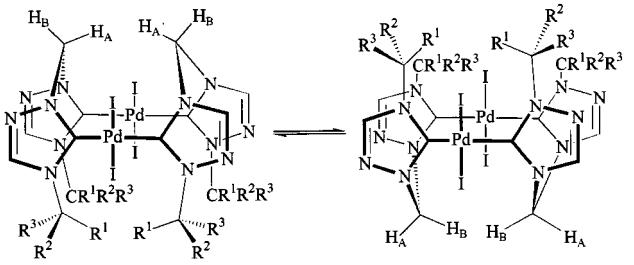
In addition, at high temperature the two doublets due to the methyl protons of the isopropyl groups (**2a**) coalesce, becoming a doublet, and the doublet of triplets due to N4−CH_2 (**2b** and **2c**) also coalesce, to give a triplet. Coalescence temperatures and free energy values[13] ($\Delta G^{\neq}$) are summarized in Table 1.

The similar free energy values obtained for each compound for the methylene bridge protons and from the substituent (N4−R) indicate that the rigid structure exhibited by the mononuclear compounds is responsible for the nonequivalence of the methylene bridge protons, the methylene protons bonded to N4 (**2b** and **2c**), and the methyl groups of the isopropyl substituents (**2a**). Therefore boat-to-boat inversion must be responsible for the equivalence of these sets of protons at higher temperatures.

The binuclear compounds **4a**−**c** also showed a dynamic behavior. In the ^{1}H NMR spectra ([D_8]THF) the methylene bridge protons give rise to a very broad singlet at room temperature which becomes sharper at high temperature and resolves into an AB system at low temperature. This is in agreement with a structure that shows a boat-to-boat-like inversion at room temperature, as outlined in Scheme 4; this inversion could be stopped at low temperature. Moreover, the broad singlet for the N4−CH_2 group of **4b** and **4c** (δ = 4.50 and 4.40, respectively) appeared as two broad signals at low temperature (two doublets of triplets were expected, but broad signals were observed probably due to a loss of resolution in the NMR apparatus at this temperature). In addition, an AB system appeared for the N4−CH_2 group in **4b** and **4c** upon irradiation, at low temperature, at the frequencies of the methylene protons in the 2-position of the chain (N4$CH_2C\mathit{H}_2$) for butyl (**4b**, δ = 2.13) and octyl (**4c**, δ = 2.15) substituents. On the other hand, it was not possible to study the dynamic behavior of **4a** by studying the methyl groups due to the fact that the two doublets expected at low temperature were not observed, again probably because of a loss of resolution in the

Table 1. Coalescence temperatures and free energy values[13] ($\Delta G^{\neq}$)

	AB System		N4−CH_2 or N4−CH_3	
Compound	Coalesc. T (K)	$\Delta G^{\neq}$ (kcal/mol)	Coalesc. T (K)	$\Delta G^{\neq}$ (kcal/mol)
2a	413	19.69	393	19.31
2b	393	18.69	398	18.70
2c	398	18.94	403	18.95
4a	288	12.54	–	–
4b	298	12.99	278	12.69
4c	293	12.78	273	12.42



2a: R^1 = H, R^2 = R^3 = Methyl
2b: R^1 = R^2 = H, R^3 = Propyl
2c: R^1 = R^2 = H, R^3 = Heptyl

Scheme 4. Conformational inversion of **4a**−**c**

NMR apparatus. Coalescence temperatures and free energy values[13] ($\Delta G^{\neq}$) are summarized in Table 1.

We can draw similar conclusions for the binuclear compounds **4a**−**c**. Free energy values indicate that the rigid structure at low temperature is responsible for the nonequivalence of the methylene bridge protons, the nonequivalence of the methylene protons bonded to N4 (**4b** and **4c**), and therefore the inversion at room temperature makes them equivalent.

Experimental Section

General considerations: All operations were performed under an inert atmosphere using standard vacuum line techniques. Solvents were purified by distillation from appropriate drying reagents before use. 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. IR spectra were recorded (in the region between 4000 and 200 cm^{-1}) on a Perkin−Elmer PE 883 IR spectrophotometer in KBr. NMR spectra were recorded on a Varian Unity 300. Chemical shifts are expressed in parts per million (δ) relative to TMS as internal standard in [D_6]DMSO. FAB-MS were recorded on a VG Autospect instrument using *m*-nitrobenzylalcohol as matrix. CI-MS were recorded on a NERNAG R10−10H instrument in NH_3 or CH_4. The 1,1′-Methylenebis(4-alkyl-1,2,4-triazolium) diiodides (**1a**−**c**) were prepared as previously reported.[10]

Preparation of 1,1′-methylenebis(4-methyl-1,2,4-triazolium) diiodide (1d): A mixture of 1,1′-methylenebis(1,2,4-triazole)[10] (100 mg, 0.67 mmol) and an excess of methyl iodide (15 mL) was stirred and heated at 130°C for 10 h in a 50 mL Fisher−Porter bottle. After cooling, the suspended solid was isolated by filtration, washed with ethyl acetate and recrystallized from ethanol. Yield: 87%; m.p. 211−213°C (decomposition). − ^{1}H NMR: δ = 3.97 (s, 6 H, CH_3), 7.17 (s, 2 H, CH_2), 9.29 (s, 2 H) and 10.39 (s, 2 H) (H3 and H5). − ^{13}C{1H} NMR: δ = 34.6 (CH_3), 62.2 (CH_2), 145.5, 146.4 (C3 and C5). − $C_7H_{12}I_2N_6$ (434.02): calcd C 19.37, H 2.79, N 19.36; found C 18.95, H 3.09, N 19.41.

General Procedure for Preparation of Mononuclear Complexes (2a−c, 3): A suspension of the corresponding 1,1′-methylenebis(4-alkyl-1,2,4-triazolium) diiodide (**1a**−**d**) (0.44 mmol) and palladium acetate (89.7 mg, 0.40 mmol) in THF (250 mL) in an 1 L Schlenk tube was stirred at 0°C for between 4 and 48 h. The crude mixture was filtered and the solvent was evaporated under vacuum. Pure products were isolated as indicated in each case.

Preparation of [PdI_2(mbidty)] (2a): The general procedure for mononuclear complexes was followed. Reaction time was 24 h. The pure product was obtained as a yellow solid after washing with chloroform. Yield: 97%; m.p. 318−320°C (decomposition). − ^{1}H NMR: δ = 1.33 (d, *J* = 6.7 Hz, 6 H, CH_3), 1.53 (d, *J* = 6.7 Hz, 6 H, CH_3), 5.41 (sep, *J* = 6.7 Hz, 2 H, C*H*Me_2), 6.50 and 6.92 (AB system, *J* = 13.9 Hz, 2 H, NCH_2N), 9.12 (s, 2 H, H3). − ^{13}C{^{1}H} NMR: δ = 21.0 (CH_3), 23.4 (CH_3), 52.7 (*C*HMe_2), 66.6 (NCH_2N), 142.3 (C3), 166.7 (C5). − MS (FAB$^+$); *m*/*z* (%): 467 (37) [M + 1 − HI]$^+$, 594 (10) [M]$^+$, 701 (5) [2M − Pd − 3I]$^+$, 1060 (8) [2M − HI]$^+$. − MS (CI, NH_3); *m*/*z* (%): 251 (100) [M + 1 + NH_4 − Pd − 2HI]$^+$, 467 (18) [M + 1 − HI]$^+$, 484 (8) [M + NH_4 − HI]$^+$, 612 (44) [M + NH_4]$^+$. − $C_{11}H_{18}I_2N_6Pd$ (594.53): calcd C 22.22, H 3.05, N 14.14; found C 22.21, H 3.03, N 13.86.

Preparation of [PdI_2(mbbdty)] (2b): The general procedure for mononuclear complexes was followed. Reaction time was 4 h. The pure product was obtained as an orange solid after recrystallization from dichloromethane/diethyl ether. Yield: 95%; m.p. 295−297°C (decomposition). − ^{1}H NMR: δ = 0.87 (t, *J* = 7.3 Hz, 6 H, CH_3), 1.20 (sxt, *J* = 7.3 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 1.79 (m, *J* = 6.9 Hz, 4 H, $NCH_2CH_2CH_2CH_3$), 4.18 (dt, *J* = 13.4 Hz, *J* = 7.1 Hz, 2 H, one H from each $NCH_2CH_2CH_2CH_3$), 4.80 (dt, *J* = 13.4 Hz, *J* = 7.1 Hz, 2 H, one H from each $NCH_2CH_2CH_2CH_3$), 6.55 and 6.96 (AB system, *J* = 14.0 Hz, 2 H, NCH_2N), 8.92 (s, 2 H, H3). − ^{13}C{^{1}H} NMR: δ = 13.3 (CH_3), 18.7 ($NCH_2CH_2CH_2CH_3$), 31.8 ($NCH_2CH_2CH_2CH_3$), 48.9 ($NCH_2CH_2CH_2CH_3$), 66.7 (NCH_2N), 144.7 (C3), 166.3 (C5). − MS (FAB$^+$); *m*/*z* (%): 495 (100) [M + 1 − HI]$^+$, 621 (15) [M − 1]$^+$, 757 (11) [2M − Pd − 3I]$^+$, 1118 (40) [2M + 2 − HI]$^+$. − MS (CI, NH_3); *m*/*z* (%): 278 (11) [M + NH_4 − Pd − 2HI]$^+$, 512 (3) [M + NH_4 − HI]$^+$, 640 (100) [M + NH_4]$^+$. − $C_{13}H_{22}I_2N_6Pd$ (622.59): calcd C 25.08, H 3.56, N 13.50; found C 24.67, H 3.44, N 13.54.

Preparation of [PdI_2(mbodty)] (2c): The general procedure for mononuclear complexes was followed. Reaction time was 4 h. The pure product was obtained as an orange solid after recrystallization from diethyl ether and washing with cold diethyl ether. Yield: 100%; m.p. 304−306°C (decomposition). − ^{1}H NMR: δ = 0.84 (t, *J* = 6.6 Hz, 6 H, CH_3), 1.12−1.34 [m, 20 H, $NCH_2CH_2(CH_2)_5CH_3$], 1.70−1.92 [m, 4 H, $NCH_2CH_2(CH_2)_5CH_3$], 4.18 [dt, *J* = 13.6 Hz, *J* = 7.1 Hz, 2 H, one H from each $NCH_2CH_2(CH_2)_5CH_3$], 4.78 [dt, *J* = 13.6 Hz, *J* = 7.1 Hz, 2 H, one H from each $NCH_2CH_2(CH_2)_5CH_3$], 6.53 and 6.95 (AB system, *J* = 14.0 Hz, 2 H, NCH_2N), 8.90 (s, 2 H, H3). − ^{13}C{^{1}H} NMR: δ = 13.9 (CH_3), 22.0, 25.6, 28.4, 28.5, 29.9, 31.2 [$NCH_2(CH_2)_6CH_3$], 49.2 [$NCH_2(CH_2)_6CH_3$], 66.7 (NCH_2N), 144.8 (C3), 166.3 (C5). − MS (FAB$^+$); *m*/*z* (%): 607 (100) [M + 1 − HI]$^+$, 735 (15) [M + 1]$^+$, 981 (59) [2M − Pd − 3I]$^+$, 1342 (93) [2M + 2 − HI]$^+$, 1470 (18) [2M + 2]$^+$. − MS (CI, NH_3); *m*/*z* (%): 607 (2) [M + 1 − HI]$^+$, 626 (3) [M + 2 + NH_4 − HI]$^+$, 734 (2) [M]$^+$, 752 (100) [M + NH_4]$^+$. − $C_{21}H_{38}I_2N_6Pd$ (734.80): calcd C 34.33, H 5.21, N 11.44; found C 33.97, H 5.37, N 11.74.

Preparation of [Pd(OAc)(mbmdty)]I (3): The general procedure for mononuclear complexes was followed. Reaction time was 48 h. The crude mixture was extracted with dichloromethane and was filtered, the solvent was evaporated under vacuum and an oil was obtained. The product was isolated as a brown solid after washing with cold chloroform and crystallized together with one molecule of palladium(II) iodide. Yield: 45%; m.p. 309−311°C. − IR: $\tilde{\nu}$ = 1408 cm^{-1} (ν_s CO_2^-), 1540 cm^{-1} (ν_a CO_2^-). − ^{1}H NMR: δ = 1.87 (s, 3 H, CH_3COO), 3.89 (s, 6 H, NCH_3), 6.94 and 7.56 (AB system, *J* = 14.6 Hz, 2 H, NCH_2N), 8.95 (s, 2 H, H3). − ^{13}C{^{1}H} NMR:

δ = 23.6 (CH_3COO), 35.8 (NCH_3), 65.0 (NCH_2N), 147.0 (C3), 152.0 (C5), 181.7 (CH_3COO). − MS (FAB^+); *m/z* (%): 343 (18) [M − I]$^+$, 411 (5) [M − OAc]$^+$. − MS (CI, CH_4); *m/z* (%): 343 (5) [M − I]$^+$, 411 (10) [M − OAc]$^+$. − MS (Electrospray); *m/z* (%): 284 (17) [M − I − OAc]$^+$, 343 (100) [M − I]$^+$, 411 (66) [M − OAc]$^+$. − $C_9H_{13}IN_6O_2Pd{\cdot}PdI_2$ (470.57): calcd C 13.01, H 1.58, N 10.12; found C 13.31, H 1.43, N 10.19.

General Procedure for the Preparation of Binuclear Complexes (4a−c): A THF (15 mL) solution of the mononuclear complex (**2a−c**) (0.20 mmol) was stirred and heated at 160°C in a 50 mL Fisher−Porter bottle for between 24 and 72 h. After cooling, the solution was filtered and solvent was evaporated under vacuum to give an oil. Pure products were isolated as indicated in each case.

Preparation of $[PdI_2(\mu\text{-mbidty})]_2$ (4a): The general procedure for binuclear complexes was followed. The reaction time was 24 h. The crude material was extracted with dichloromethane, filtered, the solvent was evaporated under vacuum and an oil was obtained. The pure product was isolated as a yellow solid after washing with diethyl ether. Yield: 90%; m.p. 321−323°C (decomposition). − ^{1}H NMR: δ = 1.55 (d, *J* = 6.8 Hz, 24 H, CH_3), 5.31 (sep, *J* = 6.8 Hz, 4 H, NC*H*Me_2), 6.60−7.60 (br s, 4 H, NCH_2N), 9.26 (s, 4 H, H3). − ^{13}C{^{1}H} NMR: δ = 25.1 (CH_3), 52.6 (*C*HMe_2), 67.0 (NCH_2N), 143.5 (C3), 172.0 (C5). − MS (FAB^+); *m/z* (%): 809 (25) [M + 1−3I]$^+$, 935 (24) [M-2I]$^+$, 1063 (68) [M + 1−I]$^+$, 1191 (10) [M + 2]$^+$. − MS (CI, NH_3); *m/z* (%): 706 (100) [M + 4 − Pd − 3I]$^+$, 1063 (28) [M + 1 − I]$^+$. − $C_{22}H_{36}I_4N_{12}Pd_2$ (1189.06): calcd C 22.22, H 3.05, N 14.14; found C 22.52, H 3.38, N 14.03.

Preparation of $[PdI_2(\mu\text{-mbbdty})]_2$ (4b): The general procedure for binuclear complexes was followed. The reaction was complete after 24 h. The pure product was isolated as a yellow solid after washing with cold dichloromethane. Yield: 100%; m.p. 302−304°C (decomposition). − ^{1}H NMR: δ = 0.91 (t, *J* = 7.2 Hz, 12 H, CH_3), 1.30 (sxt, *J* = 7.4 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 2.02 (qui, *J* = 7.4 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 4.40−4.60 (br s, 8 H, $NCH_2CH_2CH_2CH_3$), 6.80−7.80 (br s, 4 H, NCH_2N), 9.03 (s, 4 H, H3). − ^{13}C{^{1}H} NMR: δ = 13.3 (CH_3), 19.0 ($NCH_2CH_2CH_2CH_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 48.8 ($NCH_2CH_2CH_2CH_3$), 67.2 (NCH_2N), 145.7 (C3), 171.3 (C5). − MS (FAB^+); *m/z* (%): 367 (13) [(M/2) − 1 − 2I]$^+$, 867 (11) [M + 3 − 3I]$^+$, 992 (18) [M + 1 − 2I]$^+$, 1119 (100) [M + 1 − I]$^+$. − MS (CI, NH_3); *m/z* (%): 1119 (100) [M + 1 − I]$^+$, 1264 (4) [M + 1 + NH_4]$^+$. − $C_{26}H_{44}I_4N_{12}Pd_2$ (1245.17): calcd C 25.08, H 3.56, N 13.50; found C 25.43, H 3.42, N 13.30.

Preparation of $[PdI_2(\mu\text{-mbodty})]_2$ (4c): The general procedure for binuclear complexes was followed. Reaction time was 72 h. The crude material was extracted with dichloromethane, the solvent was evaporated under vacuum and an oil was obtained. The pure product was isolated as a yellow solid after crystallization from cold diethyl ether. Yield: 90%; m.p. 268−270°C. − ^{1}H NMR: δ = 0.83 (t, *J* = 6.3 Hz, 12 H, CH_3), 1.10−1.30 [m, 40 H, $NCH_2CH_2(CH_2)_5CH_3$], 1.90−2.10 [br s, 8 H, NCH_2CH_2-$(CH_2)_5CH_3$], 4.30−4.50 [br s, 8 H, $NCH_2CH_2(CH_2)_5CH_3$], 6.80−7.80 (br s, 4 H, NCH_2N), 9.02 (s, 4 H, H3). − ^{13}C{^{1}H} NMR: δ = 13.9 (CH_3), 22.0, 26.0, 28.6, 29.3, 31.2 [$NCH_2(CH_2)_6CH_3$], 49.1 [$NCH_2(CH_2)_6CH_3$], 67.3 (NCH_2N), 145.8 (C3), 171.5 (C5). − MS (FAB^+); *m/z* (%): 477 (73) [(M/2)-3−2I]$^+$, 981 (20) [M − 1 − Pd − 3I]$^+$, 1089 (29) [M + 1 − 3I]$^+$, 1215 (8) [M − 2I]$^+$, 1343 (100) [M + 1 − I]$^+$, 1469 (6) [M]$^+$. − MS (CI, CH_4); *m/z* (%): 608 (100) [(M/2) − I]$^+$, 735 (16) [(M/2) + 1]$^+$, 1344 (7) [M + 2 − I]$^+$, 1470 (1) [M + 1]$^+$. − $C_{42}H_{76}I_4N_{12}Pd_2$ (1469.60): calcd C 34.33, H 5.21, N 11.44; found C 34.20, H 5.61, N 11.69.

X-ray Crystal Structure Determination for 2a: $C_{15}H_{26}I_2N_6OPd$, M = 666.62, orthorhombic, Pnma, *a* = 14.347(2) Å, *b* = 13.029(1) Å, *c* = 11.482(2) Å, *V* = 2146.3(5) Å^3, *Z* = 4, ρ_c 2.063 Mg m^{-3}, *F(000)* = 1272, λ = 0.71073 Å, T = 173(2) K, μ (Mo Kα) = 3.757 mm^{-1}, crystal size 0.7 × 0.6 × 0.5 mm, 2.84° < &*Theta;* < 24.28°, 16230 reflections (1778 independent, R_{int} = 0.0394) were collected at low temperatures using an oil-coated shock-cooled crystal[14] on a STOE-IPDS diffractometer. A numerical absorption correction was employed and the min./max. transmissions are 0.4539 and 0.5424. The structure was solved by direct methods (SHELXS-97)[15] and 144 parameters using 13 restraints were refined using the least-squares method on F^2.[16] Largest electron density residue: 0.558 e Å^{-3}, R_1 [for $F>2\sigma(F)$] = 0.025 and wR_2 = 0.060 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. A mirror plane leads to the disorder of a noncoordinated molecule of THF, which is refined anisotropically by ignoring the symmetry (PART-1) using ADP and distance restraints.

X-ray Crystal Structure Determination for 4c: $C_{49}H_{80}I_4N_{12}Pd_2$, M = 1557.65, monoclinic, I2/a, *a* = 17.410(3) Å, *b* = 18.417(3) Å, *c* = 38.870(9) Å, β = 93.74(2)°, *V* = 12437(4) Å^3, *Z* = 8, ρ_c = 1.664 Mg m^{-3}, *F(000)* = 6096, λ = 0.71073 Å, T = 173(2) K, μ(Mo-K_α) = 2.604 mm^{-1}, crystal size 0.2 × 0.2 × 0.02 mm, 1.88° < θ < 21.26°, 50565 reflections (6913 independent, R_{int} = 0.2406) were collected at low temperatures using an oil-coated shock-cooled crystal[14] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[15] and 607 parameters using 640 restraints were refined using the least-squares method on F^2.[16] Largest electron density residue: 2.142 e Å^{-3}, R_1 [for $F>2\sigma(F)$] = 0.101 and wR_2 = 0.285 (all data) with $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. The high freedom of movement of the octyl substituents combined with the poor quality and small size of the crystals led to some problems with the refinement of **4c**. An absorption correction was not possible. The heart of the molecule is very clear and easy to refine, but it is very difficult to localize the positions of the carbon atoms of the chains. For this reason the values of *R*, R_1 and wR_2 are poor.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117654 (**2a**) and CCDC-117655 (**4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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