

A hexacarbene complex derived from 1,1'-methylenebis(4-butyl-1*H*-1,2,4-triazolium) diiodide. Synthesis, characterization and catalytic activity

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Abstract

The synthesis and characterization of a hexacarbene complex (**1**) derived from 1,1'-methylenebis(4-butyl-1*H*-1,2,4-triazolium) diiodide are reported. The organic backbone was constructed prior to the introduction of metal atoms by reaction with palladium(II) acetate. The catalytic activity of **1** in a Heck reaction has been tested. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1,2,4-Triazole-5-ylidene; Carbene; Palladium; Catalysis

1. Introduction

In the past decade, significant effort has been directed towards the theoretical understanding [1], synthesis, metal coordination and catalytic applications of *N*-heterocyclic carbenes [2]. A special issue covering all previous studies and approaches has been published [3]. A large number of papers related to free carbenes and carbene complexes based on imidazole and imidazolidine rings have also been published [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. Despite the fact that several stable free imidazole-2-ylidenes are known, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene is the only 1,2,4-triazole derivative to have been isolated as the free carbene [5]. Several rhodium, ruthenium, and *cis*- and *trans*-palladium complexes derived from 4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene have been prepared [6] as well as one tungsten compound with a similar structure to the chelate carbene complexes derived from 1,1'-methylenebis(4-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-

ylidene) [7] 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 [8]. A biscarbene derived from 1*H*-1,2,4-triazole has been used in the preparation of a polymeric silver complex [9]. In 1999 we reported on some mononuclear and dinuclear palladium(II) carbene complexes derived from 1,1'-methylenebis(4-alkyl-1,2,4-triazolium) diiodides [10].

Two important reviews focused on the dendritic catalyst have recently been published by van Leeuwen and Astruc [11]. In these are described the inherent advantages associated with this type of catalysts. The active catalytic center in a metallodendrimer can be situated in three different areas: (i) metal atom as the dendrimer core, (ii) metal atoms in the dendrimer branches, and (iii) metal atoms in the periphery. The synthesis of the third type of metallodendrimer may be undertaken by two strategies. Firstly, it is possible to build the dendrimer and then incorporate the metal atoms in the final stage or, secondly, the metal atoms can be incorporated within the molecular fragments used to build the dendrimer.

We report here an example involving the use of the first method to build a dendritic catalyst bearing palladium(II)-stabilized peripheral carbene atoms.

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2. Results and discussion

The synthesis of compound **1** was accomplished through the following sequence of reactions: (i) preparation of bis(1,2,4-triazol-1-yl)methane derivative **2**; (ii) coupling with 1,3,5-trischlorocarbonylbenzene; (iii) alkylation with butyl tosylate; (iv) exchange of tosylate by iodide anions; and (v) treatment of the hexa-salt **5** with palladium(II) acetate.

Compound **2**, 4-[bis(1,2,4-triazol-1-yl)methyl]phenol, was prepared by heating a mixture of 4-hydroxybenzaldehyde dimethyl acetal [12] and 1,2,4-triazole at 120 °C without solvent for 4.5 h according to literature procedures [13]. Condensation of **2** with 1,3,5-trischlorocarbonylbenzene [14] afforded compound **3**, which can be regarded as a first generation dendrimer. Reaction of the hydroxyl group of compound **2** with appropriate AB₂-type monomers can be employed to build higher dendrimers [15].

Unexpectedly [16], the alkylation of compound **3** with alkyl iodides failed, although the use of butyl tosylate did afford the hexa-1,2,4-triazolium tosylate **4** in 70% yield.

Anion exchange was performed by stirring hexa-tosylate **4** with lithium iodide at room temperature for 1 h in THF. Filtration gave hexa-iodide **5** in 80% yield.

Reaction of hexa-iodide **5** with palladium(II) acetate in THF at 0 °C, following the procedure previously reported by us [10] for the synthesis of 1,1'-methylene-bis(4-alkyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)diiodo-

dopalladium(II), afforded the hexa-carbene **1** in 82% yield (Scheme 1).

All intermediate compounds (**2**, **3**, **4**, and **5**) were fully characterized by ¹H- and ¹³C-NMR spectroscopy, MS and microanalysis.

Compound **1** is a yellow solid and was fully characterized by ¹H- and ¹³C-NMR spectroscopy and MS. The ¹H- and ¹³C-NMR spectra are consistent with the proposed structure. The ¹H-NMR spectrum shows the signals (δ , ppm) for the hydrogen atoms of the core (9.03), the *para*-system (7.52, 7.65), the hydrogen of the bridge between the 1,2,4-triazole rings (8.41), H-3 of the 1,2,4-triazole ring (9.06) and the hydrogen atoms of the aliphatic chains (0.89, 1.23, 1.84, 4.20 and 4.89). ¹³C resonances (δ , ppm) of the significant carbon atoms are 78.3 for the carbon of the bridge, 145.1 for C-3 in the heterocyclic moiety and 166.5 for the carbene atom.

In our previous work [10], compounds **6a** and **6b** (Fig. 1) were fully characterized, including an X-ray structure of **6a**. Comparison of the significant ¹H and ¹³C resonances of compound **1** with those of **6a** and **6b** can be made from the data in Table 1. Examination of the chemical shifts for the two compounds allows us to confirm the structure of **1**.

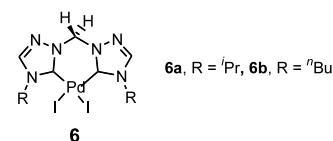
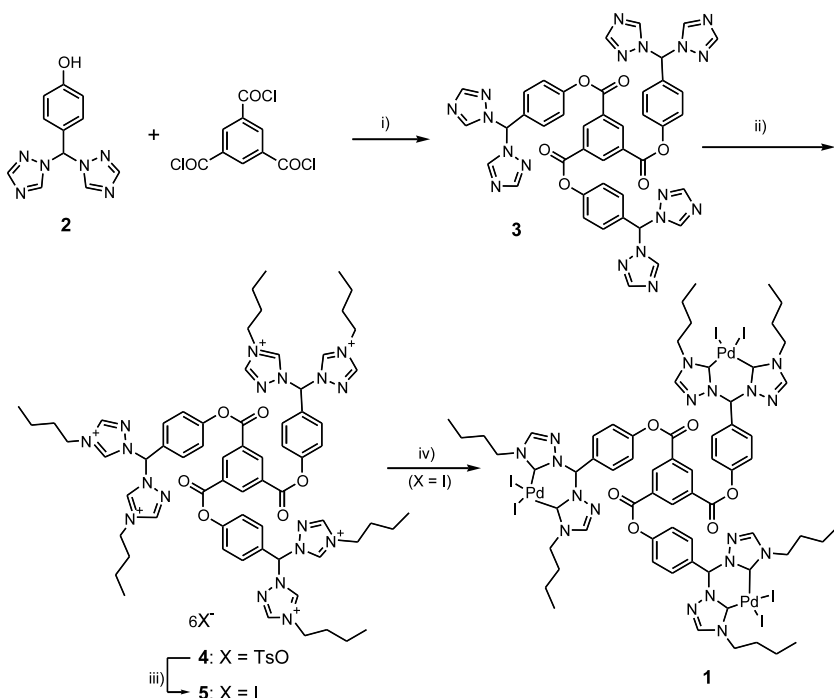


Fig. 1. Reported structure for **6a** and **6b**.



Scheme 1. Synthesis of the hexacarbene **1**. i) DMAP, THF, r.t., 2 h. ii) *n*-BuOTs, 100 °C, 24 h. iii) LiI, THF, r.t., 30 min, twice. iv) Pd(OAc)₂, THF, 0 °C, 24 h.

Table 1
Chemical shifts (δ , ppm) for representative atoms of compounds **1**, **6a** and **6b**

Group	1	6a	6b
H-3	9.06	9.12	8.92
N-CH ₂	4.20 and 4.89	–	4.18 and 4.80
C-3	145.1	142.3	144.7
Carbene C	166.5	166.7	166.3
N-CH ₂	49.5	–	48.9

The catalytic activity of hexacarbene **1** was tested by reacting *p*-bromobenzaldehyde and *n*-butyl acrylate under Heck conditions following a procedure similar to that reported by Herrmann [17]. The use of 0.16% mol of compound **1** as a catalyst gave a conversion of 74% after 5 h. Under the same reaction conditions 0.5% mol of **6b**, a palladium(II) biscarbene whose structure is comparable to the palladacycle moieties of hexacarbene **1**, gave rise to a conversion of only 50% in the same time. The two reactions attain a conversion of 100% after 8 and 50 h, respectively. The hexacarbene, which has a structure related to dendrimers, showed better catalytic activity than the monomeric catalyst (Scheme 2).

3. Experimental

Solvents were purified by distillation from appropriate drying agents 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. NMR spectra were recorded on a Varian Unity spectrometer operating at 299.980 MHz for ¹H and 75.423 MHz for ¹³C. Chemical shifts are expressed in parts per million (δ) relative to Me₄Si as internal standard. The resonances of compounds were assigned by difference NOE and Hetcor experiments.

3.1. 4-[Bis(1,2,4-triazol-1-yl)methyl]phenol (**2**)

A mixture of 2.76 g (40 mmol) of 1*H*-1,2,4-triazole, 3.36 g (20 mmol) of *p*-hydroxybenzaldehyde dimethylacetal [14] and 34 mg (0.2 mmol) of monohydrated *p*-toluenesulfonic acid was heated to 120 °C. Further quantities of monohydrated *p*-toluenesulfonic acid (34 mg, 0.2 mmol) were added every 15 min until a reaction time of 4.5 h had been reached. The mixture was cooled to room temperature (r.t.) and was extracted with

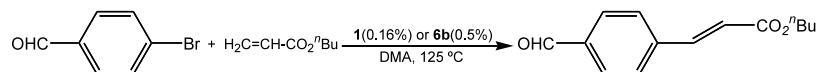
EtOAc. The organic solvent was evaporated to give a yellow oil, which was purified by chromatography (SiO₂, hexane–EtOAc, 1:3). Crystallization of the product from EtOAc–carbon tetrachloride–Et₂O–hexane yielded colorless crystals. Yield: 2.31 g (9.54 mmol), 48%. m.p.: 158–160 °C. ¹H-NMR (Me₂SO-*d*₆, δ , ppm): 6.83 (A of ABq, *J* = 8.7 Hz, 2H) and 7.25 (B of ABq, *J* = 8.7 Hz, 2H) (OC₆H₄), 8.11 (s, 2H) and 8.65 (s, 2H) [H3(Tz) and H5(Tz)], 8.23 (s, 1H, CHTz₂), 9.86 (broad s, 1H, OH). ¹³C-NMR (Me₂SO-*d*₆, δ , ppm): 72.1, 115.6, 123.9, 129.2, 144.5, 152.3, 158.6. EIMS, *m/z*: 242 [M]⁺, 174, 120, 93, 65. Anal. Calc. for C₁₁H₁₀N₆O (242.24): C, 54.24; H, 4.16; N, 34.69. Found: C, 54.26; H, 3.83; N, 35.09%.

3.2. Tris{4-[bis(1,2,4-1*H*-triazol-1-yl)methyl]phenyl}benzene-1,3,5-tricarboxylate (**3**)

A mixture of 400 mg (1.65 mmol) of compound **2** and 220 mg (1.8 mmol) of 4-dimethylaminopyridine was dissolved in 10 ml of anhyd. THF under Ar in a 100 ml Schlenk tube. After 5 min, a solution of 133 mg (0.5 mmol) of 1,3,5-trischlorocarbonylbenzene in 5 ml of anhyd. THF was added and the reaction mixture was stirred for 2 h at r.t. The amine hydrochloride was filtered off and the solvent from the filtrate was evaporated. The solid residue was dissolved in CH₂Cl₂ and the solution was washed with water. The organic layer was dried with anhyd. Na₂SO₄. The pure product was obtained as colorless crystals after filtration and solvent evaporation. Yield: 353 mg (0.40 mmol), 80%. m.p.: 135 °C (dec.). ¹H-NMR (Me₂SO-*d*₆, δ , ppm): 7.50 (s, 12H, OC₆H₄), 8.18 (s, 6H) and 8.78 (s, 6H) [H3(Tz) and H5(Tz)], 8.50 (s, 3H, CHTz₂), 9.02 (s, 3H, C₆H₃). ¹³C-NMR (Me₂SO-*d*₆, δ , ppm): 71.5, 122.4, 129.1, 130.7, 132.1, 135.2, 144.8, 151.1, 152.5, 162.7. MS (FAB, *m*-nitrobenzylalcohol), *m/z*: 883 [M+1]⁺, 814, 545, 244. Anal. Calc. for C₄₂H₃₀N₁₈O₆ (882.82): C, 57.14; H, 3.42; N, 28.56. Found: C, 57.41; H, 3.38; N, 28.78%.

3.3. 1,3,5-Benzenetriyltris[1,1'-(*p*-carbonyloxybenzylidene)bis(4-butyl-1*H*-1,2,4-triazolium)] hexatosylate (**4**)

A mixture of 441 mg (0.5 mmol) of compound **3** and 10 ml of butyl tosylate was stirred and heated at 100 °C for 24 h. The mixture was cooled to r.t. and poured onto cooled EtOAc (25 ml), at which point a colorless solid precipitated. The solid was filtered off, washed with cooled EtOAc and crystallized from a mixture of



Scheme 2. Heck olefination of *p*-bromobenzaldehyde with *n*-butyl acrylate catalyzed by **1** and **6b**.

EtOH–EtOAc. Yield: 785 mg (0.35 mmol), 70%. m.p. 220–222 °C. $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 0.90 (t, $J = 7.4$ Hz, 18H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.32 (sxt, $J = 7.4$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.84 (qui, $J = 7.6$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 2.28 (s, 18H, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3$); 4.31 (t, $J = 7.4$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 7.11, 7.46 (AA'BB' system, $J = 7.9$ Hz, 24H, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3$); 7.60, 7.80 (AA'BB' system, $J = 8.6$ Hz, 12H, OC_6H_4); 8.96 [s, 3H, $\text{CH}(1,2,4\text{-triazole})_2$]; 9.04 (s, 3H, C_6H_3); 9.52 (s, 6H) and 10.54 (s, 6H) (H3 and H5). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 13.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 18.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 20.8 ($p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3$); 30.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 48.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 74.1 [$\text{CH}(1,2,4\text{-triazole})_2$]; 122.7, 127.7, 130.7, 152.2 (OC_6H_4); 125.5, 128.2, 137.9, 145.5 ($p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3$); 130.7, 135.4 (C_6H_3); 145.3, 145.9 (C3 and C5); 162.8 (COO). MS (FAB $^+$, $m\text{-NBA}$), m/z (%): 57 (50), 126 (100), 230 (61), 354 (12), 2081 (3) [M-TsO^+]. $\text{C}_{108}\text{H}_{126}\text{N}_{18}\text{O}_{24}\text{S}_6$ (2252.68): Anal. Calc. for C, 57.58; H, 5.64; N, 11.19. Found: C, 57.48; H, 5.42; N, 11.52%.

3.4. 1,3,5-Benzenetriyltris[1,1'-(*p*-carbonyloxybenzylidene)bis(4-butyl-1H-1,2,4-triazolium)] hexaiodide (5)

To a mixture of 226 mg (0.1 mmol) of compound 4 and 20 ml of THF was slowly added a solution of 96 mg (0.72 mmol) of lithium iodide in 10 ml of THF. The resulting suspension was stirred for 30 min at r.t. The solid was filtered off and a further quantity of 96 mg (0.72 mmol) of lithium iodide in 20 ml of THF was added to the filtrate. The resulting suspension was stirred for 30 min at r.t. The solid was again filtered off and washed with THF (3 $\times$ 20 ml). The pure product was obtained as a yellow solid after crystallization from a mixture of MeOH–EtOAc. Yield: 159 mg (0.08 mmol), 80%. m.p. 182–184 °C. $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 0.93 (t, $J = 7.3$ Hz, 18H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.35 (sxt, $J = 7.4$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.87 (qui, $J = 7.6$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 4.34 (t, $J = 7.5$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 7.64, 7.81 (AA'BB' system, $J = 8.8$ Hz, 12H, OC_6H_4); 8.95 [s, 3H, $\text{CH}(1,2,4\text{-triazole})_2$]; 9.04 (s, 3H, C_6H_3); 9.54 (s, 6H) and 10.53 (s, 6H) (H3 and H5). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 13.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 18.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 30.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 48.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 74.2 [$\text{CH}(1,2,4\text{-triazole})_2$]; 122.7, 127.4, 130.6, 152.2 (OC_6H_4); 130.6, 135.3 (C_6H_3); 145.2, 145.8 (C3 and C5); 162.7 (COO). MS (FAB $^+$, $m\text{-NBA}$), m/z (%): 57 (36), 126 (100), 354 (15), 1858 (1) [$\text{M}-1-\text{I}^+$]. $\text{C}_{66}\text{H}_{84}\text{I}_6\text{N}_{18}\text{O}_6$ (1986.93): Anal. Calc. for C, 39.90; H, 4.26; N, 12.69. Found: C, 40.13; H, 3.97; N, 12.35%.

3.5. 1,3,5-Benzenetriyltris{[1,1'-(*p*-carbonyloxybenzylidene)bis(4-butyl-4,5-dihydro-1H-1,2,4-triazole-5-ylidene)]diiodopalladium(II)} (1)

A suspension of 199 mg (0.1 mmol) of compound 5 and 74 mg (0.33 mmol) of palladium acetate in 200 ml of THF in a 1 l Schlenk tube was stirred at 0 °C for 24 h under an Ar atmosphere. The solvent was then evaporated under vacuum. The residue was dissolved in 50 ml of MeCN, the solution was stirred for 15 min at r.t. and the solvent was evaporated under vacuum. The residue was washed with Et₂O and the product was obtained as a brown solid. Yield: 189 mg (0.08 mmol) 82%. Crystallization of the product was not possible due to decomposition. $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 0.89 (t, $J = 7.2$ Hz, 18H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.23 (sxt, $J = 7.4$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 1.84 (m, $J = 7.0$ Hz, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 4.20 (qui, $J = 6.8$ Hz, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 4.89 (bs, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 7.52, 7.65 (A₂B₂ system, $J = 8.6$ Hz, 12H, OC_6H_4); 8.41 [s, 3H, $\text{CH}(1,2,4\text{-triazole})_2$]; 9.03 (s, 3H, C_6H_3); 9.06 (s, 6H, H3). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, δ , ppm): 13.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 18.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 31.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 49.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 78.3 [$\text{CH}(1,2,4\text{-triazole})_2$]; 122.4, 127.9, 133.2, 151.2 (OC_6H_4); 130.7, 135.2 (C_6H_3); 145.1 (C3); 162.8 (COO); 166.5 (C5). MS: (MALDI), m/z (%): 693 (100), 1433 (25), 1580 (50), 2045 (20), 2172 (50), 2298 (5) [M^+].

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