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Six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl) guanidines: Synthesis, reactivity studies and structural aspects

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ABSTRACT

Six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl)guanidines, [$(ArNH)_2C{=}NAr$] (*sym* = symmetrical; Ar = 4-MeC_6H_4; LH$_2^{4\text{-tolyl}}$) of the types [(*C*,*N*)Pd(μ-OC(O)R)]$_2$ (**1** and **2**), [(*C*,*N*)Pd(μ-Br)]$_2$ (**3**), *cis*-[(*C*,*N*)PdLBr] (**4**–**7**), and [(*C*,*N*)Pd(acac)] (**8**) were prepared in high yield by established methods with a view aimed at understanding the influence of the 4-tolyl substituent of the guanidine moiety upon the solution behaviour of **1**–**8**. The composition of **1**–**8** was confirmed by elemental analysis, IR, and NMR spectroscopy, and mass spectrometry. The molecular structures of **1**–**6** were determined by single-crystal X-ray diffraction. Palladacycles **1**–**3** exist as a dimer in *transoid* conformation in the solid state while **4**–**6** exist as a monomer with *cis* configuration around the palladium atom as the Lewis base is placed *cis* to the Pd–C bond due to antisymbiosis. The NMR spectra of **1**–**8** revealed the presence of a single isomer in solution and this spectral feature is ascribed to the rapid inversion of the six-membered "[*C*,*N*]Pd" ring due to the presence of sterically less hindered and more symmetrical 4-tolyl substituent in the =NAr unit of the guanidine moiety.

1. Introduction

Six-membered [*C*,*N*] cyclopalladated imines are one of the interesting classes of palladacyclic compounds due to their (i) intriguing structural and reactivity pattern such as bridge-splitting reaction (bsr), (ii) regioselective aspects of C–H activation, and (iii) role as precatalysts for C–C coupling reactions, and photophysical properties [1–10]. We have recently reported syntheses, reactivity studies, structural aspects, and solution behaviour of five- and six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-triarylguanidines, [$(ArNH)_2C{=}NAr$] (*sym* = symmetrical; Ar = 2–RC_6H_4; R = OMe (LH$_2^{2\text{-anisyl}}$) [11] and Me (LH$_2^{2\text{-tolyl}}$) [12]). The number and nature of solution species of six-membered [*C*,*N*] cyclopalladated LH$_2^{2\text{-anisyl}}$ and LH$_2^{2\text{-tolyl}}$ varied depending upon the steric bulk and donor capability of *ortho* substituent of the aryl ring in the =NAr unit of the guanidine moiety. Herein, we extend our investigation on the synthesis, reactivity studies, structural aspects, and solution behaviour of six-membered [*C*,*N*] cyclopalladated *sym N*,*N*′,*N*″-tri(4-tolyl)guanidines, [$(ArNH)_2C{=}NAr$] (Ar = 4-MeC_6H_4; LH$_2^{4\text{-tolyl}}$) and the results emerged from our endeavour are presented in this manuscript.

2. Results and discussion

2.1. Carboxylato bridged dimeric palladacycles (1 and 2)

The reaction of Pd(OC(O)R)$_2$ (R = CF_3 and ^{t}Bu) with LH$_2^{4\text{-tolyl}}$ in 1:1 mol ratio in toluene at 70 °C for 6 h afforded **1** and **2** as greenish yellow, and pale yellow crystals in 84% and 92% yields, respectively as shown in Scheme 1.

The molecular structures of **1** and **2** are depicted in Fig. 1. Selected bond distances and bond angles are listed in Tables 1 and 2, respectively. Palladacycles **1** and **2** exist as a dimer wherein two palladium atoms are bridged by a pair of *syn*–*syn* bidentate carboxylato moiety. Palladacycle **1** revealed a pseudo C_2 symmetry while **2** displayed a crystallographic C_2 symmetry that passes vertically across the centre of the Pd···Pd vector to afford a *transoid* in–in conformation. In this conformation, the imine nitrogen bound to the palladium atom of one six-membered "[*C*,*N*]Pd" ring is located *trans* to the identical atom of the other six-membered "[*C*,*N*]Pd" ring and the ring NH proton of one six-membered "[*C*,*N*]Pd" ring points toward the identical atom of the second six-membered "[*C*,*N*]Pd" ring.

The palladium atom in **1** and **2** is surrounded by the oxygen atom of two separate carboxylato moieties, an imine nitrogen atom, and the aryl carbon atom. Further, the palladium atom revealed a distorted square planar geometry as inferred from the dihedral

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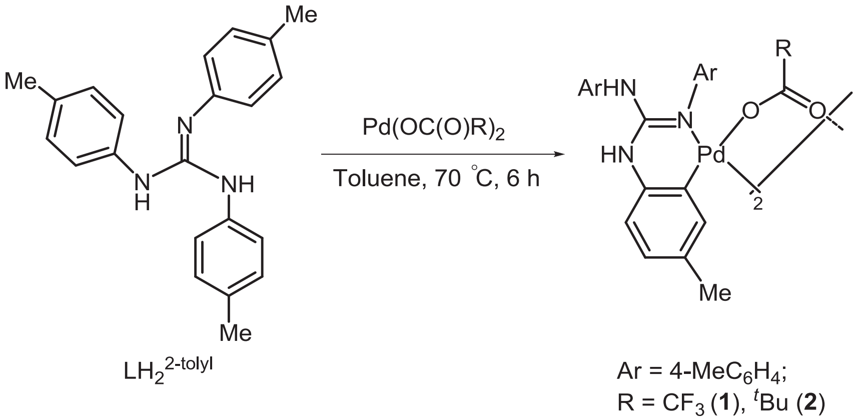

Scheme 1.

angle between two mean planes defined by N–Pd–C and O–Pd–O units (5.63(22) and 2.92(6)° (**1**); 4.84(6)° (**2**)). The six-membered "[*C*,*N*]Pd" ring exhibited a pseudo boat conformation. The bond parameters around the palladium atom in **1** and **2** are comparable with those reported for the related six-membered [*C*,*N*] cyclopalladated imines [8,11–13].

The degree of n–π conjugation involving the lone pair of the ring and exocyclic amino nitrogen atoms with C=N π* orbital of the guanidine unit can be estimated from the values of Δ_{CN} and Δ_{CN}', respectively. The Δ_{CN} value is the difference between the C=N double bond and the adjacent *endocyclic* C–N single bond distances, whereas the Δ_{CN}' value is the difference between the C=N double bond and the adjacent *exocyclic* C–N single bond distances [11]. The values of Δ_{CN} (0.047(8), and 0.036(8) Å (**1**); 0.061(6) Å (**2**)) are comparable or smaller than the values of Δ_{CN}' (0.050(8), and 0.071(8) Å (**1**); 0.069(6) Å (**2**)) and these values in turn are comparable or smaller than the values of Δ_{CN} and Δ_{CN}' observed for free guanidine, $LH_2^{4\text{-tolyl}}$ ($\Delta_{CN}' = 0.106(4)$ Å; $\Delta_{CN} = 0.077(4)$ Å) [14]. Thus, n–π conjugation involving the lone pair of the ring amino nitrogen atom with C=N π* orbital of the guanidine unit in **1** and **2** is comparable or greater than that observed with the exocyclic amino nitrogen atom. Both the amino nitrogen atoms in **1** and **2** are planar.

The ^{1}H and ^{13}C NMR spectra of **1** and **2** revealed the presence of a single isomer in solution. In principle, acetato bridged six-membered [*C*,*N*] cyclopalladated 2-benzylpyridine [15] and $LH_2^{4\text{-tolyl}}$ such as **1** and **2** can exist as a mixture of *transoid* in–in, *transoid* in–out, and *transoid* out–out conformers in solution. Further, [Pd{κ^2(*C*,*N*)–C$_6$H$_3$Me-3(NHC(NHAr)(=NAr))-2}(μ-OAc)]$_2$ (Ar = 2-MeC$_6$H$_4$; **I**), which was present in *transoid* in–in conformer in the solid state was shown to equilibrate with a small quantity of κ^2-*O*,*O*′-OAc monomeric [*C*,*N*] cyclopalladated $LH_2^{2\text{-tolyl}}$ in solution due to the presence of sterically hindered 2-tolyl substituent in the =NAr unit of the guanidine moiety [12]. It appears that the rate of six-membered "[*C*,*N*]Pd" ring inversion among three conformers mentioned above is faster than the NMR time scale due to the presence of sterically less hindered 4-tolyl substituent in the =NAr unit of the guanidine moiety of **1** and **2**. Hence, the NMR spectra of **1** and **2** apparently indicated the presence of only one isomer in solution.

2.2. Bromo bridged dimeric palladacycle (3)

Palladacycle **1** was subjected to a metathetical reaction with LiBr in aq. ethanol at 80 °C to afford **3** as yellow crystals in 94% yield as illustrated in Scheme 2. The molecular structure of **3** is practically identical to that found in [Pd{κ^2(*C*,*N*)–C$_6$H$_3$Me-3(NHC(NHAr)(=NAr))-2}(μ-Br)]$_2$ (Ar = 2-MeC$_6$H$_4$; **II** [12]) with the following exception (see the Supplementary material for the molecular structure of **3**). The [Pd(μ-Br)$_2$Pd]$^{2+}$ unit in **3** revealed a planar rhomboid conformation (Pd(1)–Br(1)–Pd(1): 95.42(1)°; Br(1)–Pd(1)–Br(1): 84.57(1)°) in contrast to the folded conformation of the same unit observed in **II** [12]. The aforementioned difference is ascribed to the presence of sterically less hindered 4-tolyl substituent in the =NAr unit of the guanidine moiety of **3**. The degree of n–π conjugation involving the lonepair of the endocyclic and the exocyclic amino nitrogen atoms with C=N π* orbital in **3** are comparable as reflected from the values of $\Delta_{CN} = 0.051(6)$ Å and $\Delta_{CN}' = 0.053(6)$ Å. Both the amino nitrogen atoms in **3** are planar.

2.3. Monomeric palladacycles (4–8)

Palladacycle **1** was subjected to the bsr with 2,6-lutidine and PTA in CH$_2$Cl$_2$ at ambient temperature to afford **4**, and **5** in 96% and 94% yields, respectively. Similarly, **3** was subjected to the bsr with 2,6-lutidine, and PTA in CH$_2$Cl$_2$ at ambient temperature to afford **6**, and **7** in 97% and 86% yields, respectively (see Scheme 3). Palladacycle **3** was treated with Na(acac) (acac = acetylacetonate) in CH$_2$Cl$_2$ at ambient temperature to afford a bis-chelated palladacycle, **8** in 97% yield as illustrated in Scheme 4.

The molecular structures of **4** and **5** are depicted in Fig. 2. Selected bond distances and bond angles are listed in Table 3. The molecular structure of **6** is practically identical to that found in [Pd{κ^2(*C*,*N*)–C$_6$H$_3$Me-3(NHC(NHAr)(=NAr))-2}Br(2,6-Me$_2$C$_6$H$_3$N)] (Ar = 2-MeC$_6$H$_4$ (**III**); see the Supplementary material for the molecular structure of **6**). Two molecules crystallized in an asymmetric unit in the case of **4** and the structural features are described here only for molecule 1. The palladium atom is surrounded by the imine nitrogen, the aryl carbon, nitrogen or phosphorus atom of the Lewis base, and oxygen atom of the TFA (**4** and **5**) or bromide (**6**). The palladium atom revealed a slightly distorted square planar geometry. The angle between NPdC and OPdE planes (*E* = N or P) in **4**–**6** are 2.79(28), 8.08(9), 11.37(17)°, respectively. The Lewis base is coordinated to the palladium atom in *cis* relation with respect to the Pd–C bond due to antisymbiosis [16]. The molecular structures of six-membered [*C*,*N*] cyclopalladated imines of the type [(*C*,*N*)PdX(phosphine)] are known to contain the phosphine in *cis* orientation with respect to the Pd–C bond [5,7,11,12] due to antisymbiosis. The six-membered "[*C*,*N*]Pd" ring in **4**–**6** adopts a pseudo boat conformation.

The Pd–C distance in **4**–**6** (1.982(5) Å (**4**), 1.978(3) Å (**5**), and 1.983(3) Å (**6**)), the Pd–N distances in **4** and **6** (Pd–N$_{guanidine}$: 2.016(4) Å (**4**), 2.038(2) Å (**6**); Pd–N$_{lutidine}$ = 2.060(4) Å (**4**), 2.049(2) Å (**6**)) are comparable with the corresponding distances observed around the palladium atom in **III** (Pd–C = 1.985(2) Å; Pd–N$_{guanidine}$ = 2.034(1) Å;