



Synthesis and structural studies of cyclopalladated complexes of secondary benzylamines

Kazem Karami^{a,*}, Mahboubeh Hosseini Kharat^a, Corrado Rizzoli^b, Janusz Lipkowski^c

^a Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Iran

^b Department of Chemistry, University of Parma, I-43124 Parma, Italy

^c Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

ARTICLE INFO

Article history:

Received 21 October 2012

Received in revised form

25 December 2012

Accepted 27 December 2012

Keywords:

Secondary benzylamines

Cyclopalladated complexes

Palladium(II) acetate

Crystal structures

ABSTRACT

Di-nuclear cyclopalladated acetato-bridged complexes derived from secondary benzylamines, $[\text{Pd}_2\{(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{R})\}_2(\mu\text{-OAc})_2]$ ($\text{R} = \text{Et}$ (**1**), $\text{R} = \text{t-Bu}$ (**2**)) were obtained by refluxing of corresponding benzylamines and $\text{Pd}(\text{OAc})_2$ in a 1:1 M ratio. Complex **1** was also prepared by heating the bis-amine complex $[\text{Pd}(\text{OAc})_2(\text{PhCH}_2\text{NH}(\text{Et}))_2]$ (**3**) in toluene at 60 °C. Complex **3** reacted with an excess of NaCl to give $[\text{Pd}(\text{Cl})_2(\text{PhCH}_2\text{NH}(\text{Et}))_2]$ (**4**). Metathetical reaction of **1** and **2** with an excess of NaCl or NaBr afforded the corresponding dimers $[\text{Pd}_2\{(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{R})\}_2(\mu\text{-X})_2]$ ($\text{X} = \text{Cl}$, $\text{R} = \text{Et}$ (**5**); $\text{X} = \text{Cl}$, $\text{R} = \text{t-Bu}$ (**6**); $\text{X} = \text{Br}$, $\text{R} = \text{t-Bu}$ (**7**)). The cationic complex $[\text{Pd}(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{Et})(\text{phen})]\text{BF}_4$ (**8**) can be obtained by reacting chloro bridge dimer **5** with AgBF_4 and 1,10-phenanthroline (phen). Neutral ligands split the halide bridges in **6** and **7** to give monomeric complexes $[\text{Pd}(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{t-Bu})\text{X}(\text{L})]$ ($\text{X} = \text{Cl}$, $\text{L} = \text{PPh}_3$ (**9**); $\text{X} = \text{Br}$, $\text{L} = \text{Me}_3\text{Py}$ (**10**)). Complexes **1–10** were fully characterized by elemental analysis, IR and NMR spectroscopies. In addition, the crystal structures of **2**, **3**, **4**, **8**, **9** and **10** were determined by single-crystal X-ray diffraction analysis. In all these structures, the palladium atom shows a distorted or slightly distorted square-planar geometry.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The interest in cyclopalladated complexes derived from N-donor ligands has increased considerably due to their extremely high catalytic activity in a variety of important C–C coupling reactions including Heck reactions, Stille coupling and Suzuki coupling [1,2]. Cyclopalladation of amine complexes is governed by a fundamental rule reported in 1968 by Cope and Friedrich [3]: direct activation of C–H bonds by palladium(II) species to afford the corresponding palladacycles is the most feasible in the case of tertiary amines, whereas primary and secondary amines are usually inert toward such activation. However, when using different palladium reagents and/or experimental reaction conditions, it has been demonstrated that benzylamine, and some of its secondary amine derivatives, can be orthometalated [4,5]. The mechanism of orthometalation of benzylamine has been investigated by Ryabov et al. [6], proposed that the cyclopalladation proceeds mainly via monomeric intermediate $[\text{Pd}(\text{OAc})_2(\text{amine})_2]$. High concentrations of amine favor

the formation of the monomeric complex. Then the intermediate transforms into orthopalladated materials. The orthopalladation of secondary amines has been reported by Fuchita et al. [4,7,8], Vicente et al. [9] and our laboratory [10]. For the first time, Vicente et al. [9] reported the crystal structure of a cyclopalladated complex of secondary benzylamine. Considering that, palladacycles of secondary amine have not received due attention than the tertiary amine, as not many crystal structures of them have been reported and due to our interest in the preparation and application of complexes containing the orthopalladated fragment of amines [10–12], we have described the synthesis and structural characterization of mono- and di-nuclear complexes from secondary benzylamines. We have also designed the synthesis of the bis-amine complex **3** to form acetato-bridged palladacycle **1** in order to compare with the case where the palladium (II) acetate reacts directly with the corresponding amine in a 1:1 M ratio to give the bridged palladacycle **1**. It should be noted that we have been previously reported the formation of acetato-bridged di-nuclear palladacycles **1** and **2** [10], but herein we describe the details of their synthesis and characterize them fully. Moreover, the crystal structure of the mononuclear complex **9**, which was previously characterized [10], is reported here.

* Corresponding author. Tel.: +98 3113913239; fax: +98 3113912350.
E-mail address: karami@cc.iut.ac.ir (K. Karami).

2. Result and discussion

Scheme 1 shows the complexes prepared in this work and the labeling assigned to the methylene and aromatic protons. The crystal data and structural refinement parameters for complexes **2**, **3**, **4**, **8**, **9** and **10** are listed in **Table 1**.

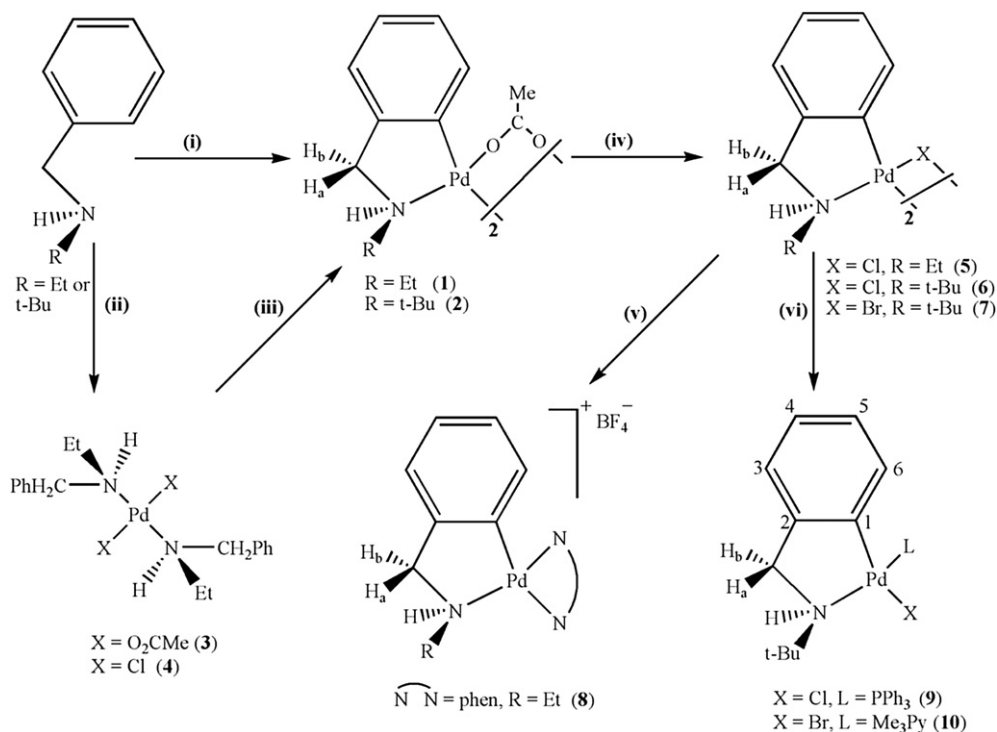
2.1. Synthesis and structure of mono- and di-nuclear complexes

The reaction of the secondary benzylamines $\text{PhCH}_2\text{NH}(\text{Et})$ or $\text{PhCH}_2\text{NH}(\text{t-Bu})$ with $\text{Pd}(\text{OAc})_2$ in a 1:1 M ratio has been carried out in toluene at 60 °C to produce five-membered palladacycles of general formula $[\text{Pd}_2\{(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{R})\}_2(\mu\text{-OAc})_2]$ ($\text{R} = \text{Et}$ (**1**), $\text{R} = \text{t-Bu}$ (**2**)). The reaction of palladium(II) acetate with $\text{PhCH}_2\text{NH}(\text{Et})$ in a 1:2 M ratio gives also the corresponding bis-amine adduct $[\text{Pd}(\text{OAc})_2(\text{PhCH}_2\text{NH}(\text{Et}))_2]$ (**3**). It has already been confirmed that if there are bulky groups around the nitrogen atom of the benzylamine, the formation of the bis-amine adduct is difficult [4]. Addition of NaCl to a methanolic solution of **3** allowed the isolation of bis(amino)-dichloro palladium(II) $[\text{Pd}(\text{Cl})_2(\text{PhCH}_2\text{NH}(\text{Et}))_2]$ (**4**). When the bis-amine complex **3** was heated in toluene at 60 °C, the di-nuclear complex **1** was precipitated but the reaction yield was low (22%). Treatment of complexes **1** and **2** with an excess of NaCl or NaBr in methanol afforded the corresponding chloro and bromo bridging dimers $[\text{Pd}_2\{(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{R})\}_2(\mu\text{-X})_2]$ ($\text{X} = \text{Cl}$, $\text{R} = \text{Et}$ (**5**); $\text{X} = \text{Cl}$, $\text{R} = \text{t-Bu}$ (**6**); $\text{X} = \text{Br}$, $\text{R} = \text{t-Bu}$ (**7**)) in good yields. Complex **5** reacted with AgBF_4 and 1,10-phenanthroline (phen) to give $[\text{Pd}(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{Et})(\text{phen})]\text{BF}_4$ (**8**). Complexes **6** and **7** reacted with PPh_3 and sym-collidine (Me_3Py) in a 1:2 M ratio to give the mononuclear complexes $[\text{Pd}(\text{C},\text{N})\text{-C}_6\text{H}_4\text{CH}_2\text{NH}(\text{t-Bu})\text{X}(\text{L})]$ ($\text{X} = \text{Cl}$, $\text{L} = \text{PPh}_3$ (**9**); $\text{X} = \text{Br}$, $\text{L} = \text{Me}_3\text{Py}$ (**10**)). The elemental analysis results of the prepared compounds **1–10** are in a good agreement with the calculated values. The mono- and di-nuclear palladacycles **1**, **2** and **5–10** were also characterized by IR and NMR spectroscopy. The

crystal structures of complexes **2**, **3**, **4**, **8**, **9** and **10** have been solved by X-ray diffraction studies.

The IR spectra of complexes **1** and **2** show characteristic bands due to the bridging acetato ligand at 1566, 1415 cm^{-1} and 1577, 1455 cm^{-1} , respectively [7]. Concerning the ^1H NMR spectrum of **1** we observe signals from the *anti* and *syn* type isomers. Two well-separated sets of signals appear for the methylene protons, acetato-methyl and *N*-ethyl protons, while signals due to the four aromatic protons of the two isomers overlapped with each other. It is confirmed that the *syn* configurations are less favorable as compared with the *anti* configurations, because two amino groups in the *syn* type are located close to each other and create steric hindrance [7]. Differently from **1**, both the acetato-methyl and *N*-tert-butyl protons in **2** appeared only as one singlet in the ^1H NMR spectrum. Considering that the tert-butyl group in **2** is bulkier than the ethyl group in **1**, it supports that **2** displays an *anti* configuration.

The crystal structure of **2** shows that the molecule possesses an approximate (noncrystallographic) C_2 symmetry with the nitrogen atoms mutually *trans* with respect to the di- μ -acetato bridges. Selected bond distances and angles are summarized in **Fig. 1**. The coordination around each palladium atoms is essentially square-planar. Each palladium center deviates very slightly (0.0278(2) Å and 0.0192(2) Å) from the planes containing O1, C1, O3, N1 and N2, O2, C12, O4, respectively. As a result of Pd1 and Pd2 being bridged by two mutually *cis* μ -acetate ligands, the chelating C,N-bonded benzylamines are forced to lie above one another in the dimeric molecule. The bridging acetato groups force the two palladium planes of the dimer to have dihedral angles of 26.64(5)°. The nonbonding Pd1...Pd2 distance of 2.9145(2) Å is a little shorter than those found in $[\text{Pd}\{\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_2\text{Ph})_2\text{-C},\text{N}\}(\mu\text{-OAc})_2]$ (I, 3.0621 Å) [4] and $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2)_2\text{NH}_2\text{-2-OMe-5-}\kappa^2\text{C},\text{N}\}(\mu\text{-OAc})_2]$ (II, 2.9229 Å) [13] because of the larger steric repulsion of the benzyl groups in I and II. The Pd–C distances (1.949(2) and 1.955(2) Å) are also shorter than those reported for I and II. The Pd–N distances (2.1069(18) and



Scheme 1. (i) $\text{Pd}(\text{OAc})_2$ in toluene at 50 °C; (ii) $1/2 \text{ Pd}(\text{OAc})_2$ in toluene; (iii) complex **1** in toluene at 50 °C; (iv) excess NaCl or NaBr in methanol; (v) complex **5**, AgBF_4 , 1,10-phenanthroline, THF; (vi) complex **6**, PPh_3 , complex **7**, Me_3Py , (dichloromethane, room temperature, 6 h).

Table 1
Crystal data and refinement parameters for complexes **2**, **3**, **4**, **8**, **9** and **10**.

| | 2 | 3 | 4 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|
| Empirical formula | C ₂₆ H ₃₈ N ₂ O ₄ Pd ₂ | C ₂₂ H ₃₀ N ₂ O ₄ Pd | C ₁₈ H ₂₆ Cl ₂ N ₂ Pd | C ₂₁ H ₂₀ BF ₄ N ₃ Pd | C ₂₉ H ₃₁ ClNPPd | C ₁₉ H ₂₇ BrN ₂ Pd |
| Formula weight | 655.38 | 494.90 | 447.71 | 507.61 | 566.37 | 469.74 |
| <i>T</i> /K | 295(2) | 100(1) | 100(1) | 100(2) | 100(1) | 292(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> -1 | <i>C</i> 2/ <i>c</i> |
| <i>a</i> /Å | 10.5589(4) | 9.6680(10) | 9.9100(1) | 10.7340(2) | 9.9070(2) | 12.1947(6) |
| <i>b</i> /Å | 17.9393(8) | 13.3890(10) | 17.8080(2) | 11.0010(1) | 14.1890(3) | 20.3995(10) |
| <i>c</i> /Å | 15.0885(6) | 9.9240(10) | 11.9460(2) | 16.9660(2) | 20.2120(4) | 17.7565(9) |
| α /° | 90 | 90 | 90 | 90 | 75.45(2) | 90 |
| β /° | 99.3223(6) | 118.12(2) | 113.010(1) | 99.074(2) | 78.76(2) | 114.7415(7) |
| γ /° | 90 | 90 | 90 | 90 | 71.23(2) | 90 |
| <i>V</i> /Å ³ | 2820.3(2) | 1132.98(18) | 1940.46(4) | 1978.35(5) | 2583.58(9) | 4011.7(3) |
| <i>Z</i> | 4 | 2 | 4 | 4 | 4 | 8 |
| μ (mm ⁻¹) | 1.307 | 0.847 | 1.232 | 0.989 | 0.901 | 2.918 |
| <i>D</i> _{cal} /Mg m ⁻³ | 1.544 | 1.445 | 1.532 | 1.704 | 1.456 | 1.55539 |
| <i>R</i> (000) | 1328 | 508 | 912 | 1192 | 1160 | 1888 |
| θ ranges/° | 6.75–24.28 | 3.03–27.73 | 2.94–28.92 | 3.04–27.24 | 3.01–28.99 | 4.27–22.64 |
| Independent reflections | 5534 | 2580 | 4768 | 3351 | 8798 | 3749 |
| Data/restraints/parameters | 5534/0/323 | 2580/0/133 | 4768/0/216 | 3351/0/283 | 8798/0/603 | 3749/0/219 |
| Goodness-of-fit on <i>F</i> ² | 1.089 | 2.499 | 1.323 | 2.062 | 0.880 | 1.028 |
| Final <i>R</i> indices | <i>R</i> ₁ = 0.0196 <i>wR</i> ₂ = 0.0514 | <i>R</i> ₁ = 0.0268 <i>wR</i> ₂ = 0.0640 | <i>R</i> ₁ = 0.0272 <i>wR</i> ₂ = 0.0606 | <i>R</i> ₁ = 0.0199 <i>wR</i> ₂ = 0.0474 | <i>R</i> ₁ = 0.0193 <i>wR</i> ₂ = 0.0471 | <i>R</i> ₁ = 0.0242 <i>wR</i> ₂ = 0.0574 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0209 <i>wR</i> ₂ = 0.0522 | <i>R</i> ₁ = 0.0316 <i>wR</i> ₂ = 0.0650 | <i>R</i> ₁ = 0.0274 <i>wR</i> ₂ = 0.0607 | <i>R</i> ₁ = 0.0222 <i>wR</i> ₂ = 0.0481 | <i>R</i> ₁ = 0.0215 <i>wR</i> ₂ = 0.0486 | <i>R</i> ₁ = 0.0301 <i>wR</i> ₂ = 0.0604 |

2.0724(18) Å) are shorter and longer than those found in **1** and **II**, respectively. These data suggest that sterically demanding benzyl groups at nitrogen atom increase the Pd–N length [4].

The molecular structures of bis-amine complexes **3** and **4** are shown in Figs. 2 and 3, respectively. Complex **3** possesses crystallographically imposed center of symmetry. In both compounds, the palladium metal is coordinated in an almost regular square planar geometry by two monodentate acetato (in **3**) or chloride (in **4**) anions, and by two nitrogen atoms from *N*-benzylethylamine ligands. The *trans* configuration assumed by the amino ligands is the normal geometry observed for bis(amino)-palladium(II) complexes [14]. In **3** the metal atom lies in plane through the donor atoms for symmetry requirements, while it is displaced by 0.0073(2) Å in **4**. As expected, the Pd–O (2.012(2) Å) bond length in **3** is significantly

shorter than those observed in **2** (mean value 2.10(3) Å) and other related benzylamine acetato-bridged complexes [4,13]. In the crystal structure of **3**, two intramolecular N–H⋯O hydrogen bonds are present. In complex **4**, molecules are linked into zig-zag chains running parallel to the *b* axis by intermolecular N–H⋯Cl hydrogen bonds.

The ¹H NMR spectra of complexes **5**–**7** show only one set of signals, which indicate that in solution the cyclopalladated dimers **5**–**7** consist of only one geometrical isomer which we propose to be the anti type isomer [15]. In di-nuclear complexes **5**–**7**, the methylene protons are diastereotopic resulting in the formation of two

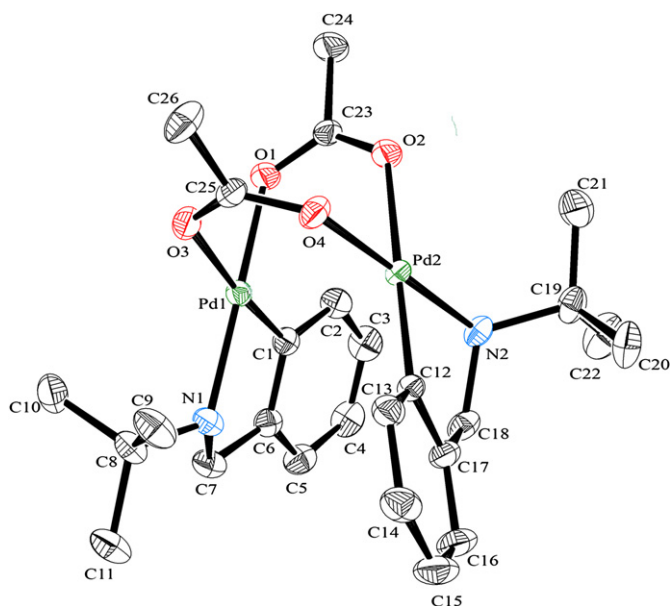


Fig. 1. X-ray thermal ellipsoid plot of complex **2**.

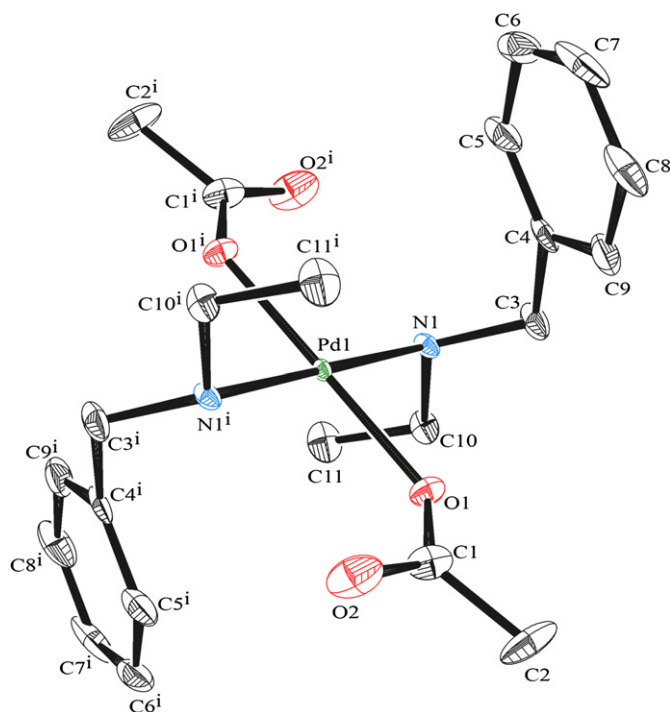


Fig. 2. X-ray thermal ellipsoid plot of complex **3**.

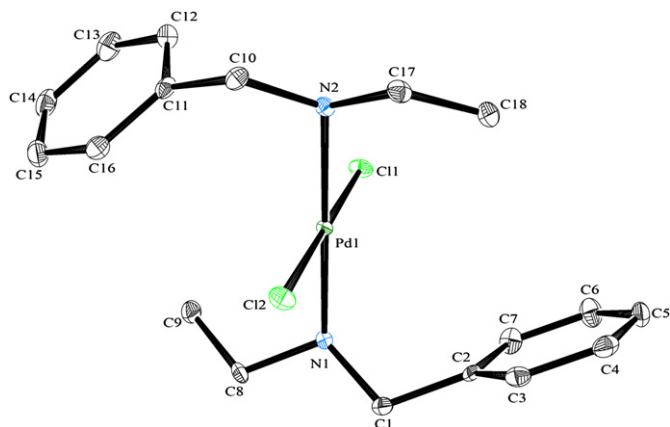


Fig. 3. X-ray thermal ellipsoid plot of complex 4.

separated signals each integrating for one proton at ~ 4.3 and ~ 3.8 ppm.

In the ^1H NMR spectra of the mononuclear complexes **8**, **9** and **10**, the methylene protons are also nonequivalent and resonate at different places. Moreover, the ^1H NMR spectra show similar patterns for the $\text{H}_3\text{--H}_5$ aromatic protons of amine, but H_6 is significantly shifted to lower frequencies for **8** (6.56 ppm), **9** (6.19 ppm) and **10** (5.49 ppm) because of the anisotropic shielding from the phenyl or pyridine ring [7].

Fig. 4 shows the ORTEP plot of complex **8** and selected bond distances and angles. The asymmetric unit of **8** consists of a complex cation and tetrafluoroborate as counter ion. The palladium metal exhibits a slightly distorted square-planar geometry (maximum deviation 0.096(2) Å for atom C15), as indicated by the angles subtended by the ligands at Pd(II) varying from 80.01(8) to 101.02(8)° and from 175.01(7) to 176.84(7)°. The summation of the bond angles around the palladium is 360.26°. The metal deviates 0.02320(14) Å from the mean coordination plane. The dihedral angle between the two planes formed by N1, Pd1, N2 and C15, Pd1, N3 is 6.25(7)°. The Pd–N2 bond distance of 2.1288(17) Å is longer than the Pd–N1 distance of 2.0568(17) Å, showing that C15 has a larger *trans* influence than N3 of the amine group. The bite angle N1–Pd–N2 is 80.16(7)°, which is normal for Pd(II) complexes containing bpy or phen ligands [16,17]. The Pd1–C15 bond distance

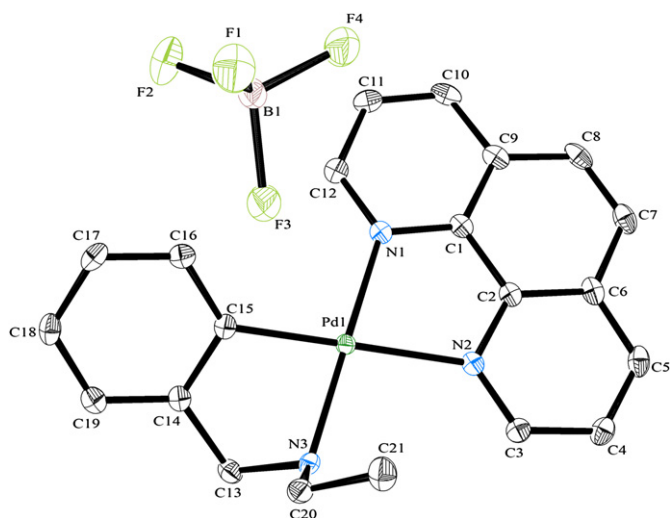


Fig. 4. X-ray thermal ellipsoid plot of complex 8.

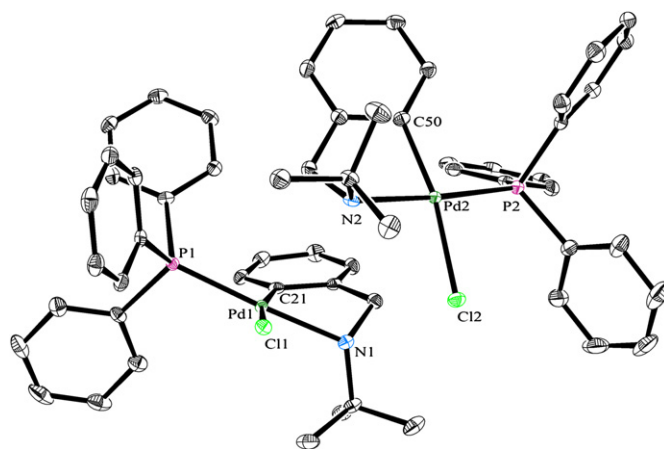


Fig. 5. X-ray thermal ellipsoid plot of the two independent molecules (A and B) of complex 9.

(1.997(2) Å) is similar to that found in a related orthopalladated complex [17].

The mononuclear complex **9** crystallizes with two independent molecules (hereafter called molecule A and B) in the asymmetric unit (Fig. 5). Each palladium metal is coordinated in a distorted square-planar geometry (maximum deviations: 0.088(2) and 0.135(2) Å for atoms C21 and C50 for molecules A and B, respectively) by a chloride anion, a P atom of a triphenylphosphine ligand and a chelating *N*-benzyl tert-butylamine- C^2, N moiety forming a five-membered cyclopalladated ring through the N1, C21 atoms for molecule A and N2, C50 atoms for molecule B. The chelate ring assumes a half-boat conformation, with atoms N1 and N2 displaced by 0.7573(16) and 0.7222(16) Å, respectively, from the Pd1/C19–C21 and Pd2/C48–C50 mean planes. The Pd–C bond distances (2.0101(18) and 2.0185(18) Å for A and B, respectively) are within the range usually reported by five- and six-membered palladacycles [18–21]. The phosphine ligand is in *trans* position to the amine group, in agreement with what observed in related mononuclear palladacycles, where the phosphine and aryl ligands have a well-demonstrated tendency not to be *trans* to each other when coordinated to palladium [18–21]. In the crystal, molecules A and B

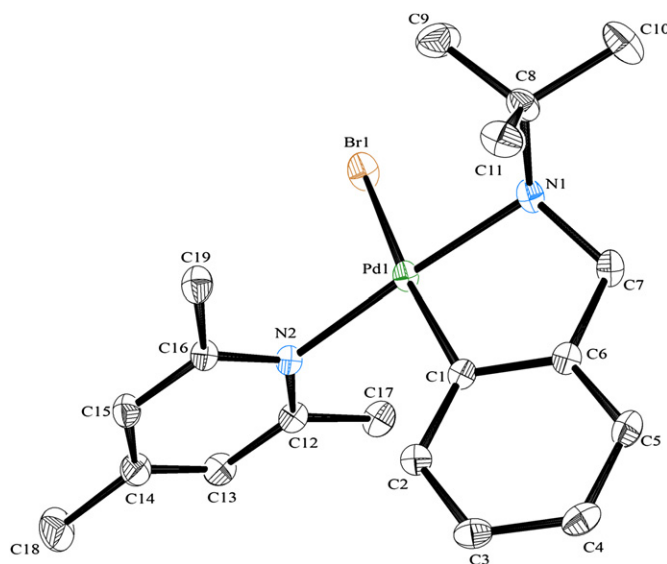


Fig. 6. X-ray thermal ellipsoid plot of complex 10.

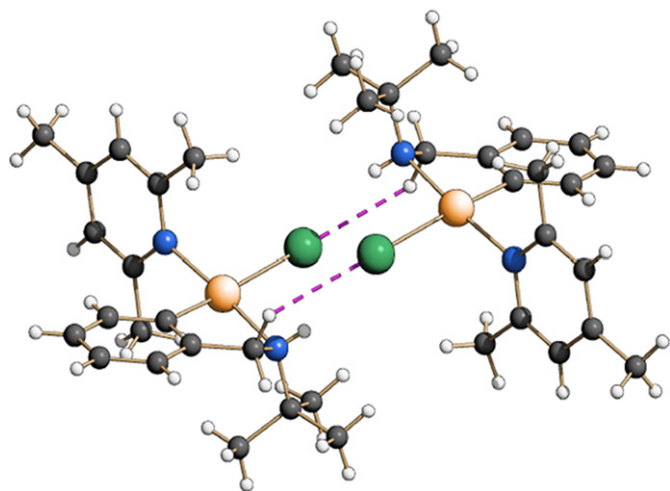


Fig. 7. Hydrogen bonding (dashed lines) between the bromine atoms and the CH₂ groups of complex **10**.

are linked by a pair of N–H···Cl hydrogen bonds resulting in the formation of a ring of $R_2^2(8)$ graph-set motif.

The crystal structure of **10** (Fig. 6) shows a significantly tetrahedrally distorted square planar environment (maximum deviation 0.143(3) Å) with a dihedral angle of 9.53(8)° between the N1, Pd1, C1 and N2, Pd1, Br1 planes. The angles around palladium deviate from the ideal value of 90° due to the small bite of the cyclometalated ligand, the C–Pd–N angle being 82.68(10)°. Comparing **9** and **10**, the Pd–N distances (2.1215(15) and 2.1375(16) Å) and the Pd–C distances (2.0101(18) and 2.0185(18) Å) for **9** are longer than the Pd–N1 distance (2.081(2) Å) and the Pd–C distance (1.983(2) Å) for **10**, due to the greater *trans* influence of the P and Cl atoms with respect to the N2 and Br1 atoms, respectively [22]. In the crystal, two molecules of complex **10** are connected through a pair of hydrogen bonds between the bromine atoms and the CH₂ groups (Fig. 7).

3. Conclusion

We present here the preparation and structures of mono- and di-nuclear palladacycles from secondary benzylamines. We have also successfully showed that the acetato-bridge palladacycle **1** is synthesized by two methods: the first, a direct reaction of palladium (II) acetate with the corresponding benzylamine and the second, from heating bis-amine complex **3**, which confirms that cyclopalladation proceed through the bis-amine adduct, although the yield of latter method was low. The structure of complexes **2**, **3**, **4**, **8**, **9** and **10** was confirmed by single-crystal X-ray diffraction. The crystal structure of **9** and **10** shows the phosphine and sym-collidine ligands are in *trans* position to the amine group.

4. Experimental

4.1. General

Starting materials and solvents were purchased from Sigma–Aldrich or Alfa Aesar and used without further purification. Infrared spectra were recorded on a FT-IR JASCO 680 spectrophotometer in the spectral range 4000–400 cm^{−1} using the KBr pellets technique. NMR spectra were measured on a Bruker spectrometer at 400.13 MHz (¹H), 100.61 MHz (¹³C) and 161.97 MHz (³¹P) using standard pulse sequences at 298 K. Elemental analysis was performed on Leco, CHNS-932 apparatus.

4.2. Synthesis of [Pd₂{(C,N)-C₆H₄CH₂NH(Et)}₂(μ-OAc)₂] (**1**)

Method (a). *N*-benzylethylamine (150 μL, 1 mmol) was added to a toluene (20 mL) solution of palladium(II) acetate (0.224 g, 1 mmol) and the resulting solution was heated under reflux for 24 h. The resulting mixture was evaporated to dryness and the residue recrystallized from CH₂Cl₂ and hexane to give **1**. Yield: 72%. IR (KBr, cm^{−1}): ν(CO) = 1566, 1413; ν(NH) = 3168. ¹H NMR (DMSO-*d*₆, ppm): δ = 0.73 (t, 3H, CH₃, ³J_{HH} = 7.2 Hz), 1.19 (t, 3H, CH₃, ³J_{HH} = 7.2 Hz), 1.8 (s, 3H, MeCO₂), 1.88 (s, 3H, MeCO₂), 2.77 (m, 4H, CH₂), 3.33 (br s, 1H, NH), 3.54 (dd, 2H, CH₂, ³J_{HH} = 4.4 Hz), 3.78 (dd, H_a, CH_aH, ²J_{HH} = 15.6 Hz, ³J_{HH} = 4.4 Hz), 4.24 (dd, H_b, CH_bH, ²J_{HH} = 14.6 Hz, ³J_{HH} = 5.6 Hz), 5.94 (br s, 1H, NH), 6.73–7.5 (m, 8H, C₆H₄, ³J_{HH} = 7.6 Hz). Anal. calcd. for C₂₂H₃₀N₂O₄Pd₂: C, 44.0; H, 5.04; N, 4.67. Found: C, 43.9; H, 5.04; N, 4.65%.

Method (b). A toluene (10 mL) solution of [Pd{PhCH₂NH(Et)}₂(OAc)₂] (**3**) (0.1 g, 0.2 mmol) was heated at 60 °C for 2 days. The precipitated green powder was collected and washed with diethyl ether to give **1** (22%).

4.3. Synthesis of [Pd₂{(C,N)-C₆H₄CH₂NH(*t*-Bu)}₂(μ-OAc)₂] (**2**)

N-benzyl tert-butylamine (181 μL, 1 mmol) was added to a toluene (20 mL) solution of palladium(II) acetate (0.224 g, 1 mmol) and the resulting solution was heated under reflux for 24 h. The resulting mixture was evaporated to dryness and the residue recrystallized from CH₂Cl₂ and hexane to give **2**. Yield: 75%. IR (KBr, cm^{−1}): ν(CO) = 1577, 1455; ν(NH) = 3218. ¹H NMR (DMSO-*d*₆, ppm): δ = 1.11 (m, 9H, *t*-Bu), 1.8 (br s, 3H, MeCO₂), 3.9 (d, H_a, CH_aH, ²J_{HH} = 15.6 Hz), 4.34 (d, H_b, CH_bH, ²J_{HH} = 15 Hz), 6.82–7.43 (m, 4H, C₆H₄), 7.69 (br s, 1H, NH); ¹³C{¹H} NMR (DMSO-*d*₆, ppm): δ = 25.03 (C, *t*-Bu), 28.6 (Me), 54.01 (MeCO₂), 56.8 (CH₂), 120.8, 124.4, 124.7, 132.6 (C_{aromatic}). Anal. calcd. for C₂₆H₃₈N₂O₄Pd₂: C, 47.6; H, 5.8; N, 4.27. Found: C, 47.5; H, 5.6; N, 4.2%.

4.4. Synthesis of [Pd{PhCH₂NH(Et)}₂(OAc)₂] (**3**)

N-benzylethylamine (300 μL, 2 mmol) was added to a toluene (20 mL) solution of palladium(II) acetate (0.224 g, 1 mmol) and the resulting solution was heated under reflux for 6 h. The resulting mixture was evaporated to dryness and the residue was precipitated from CH₂Cl₂ and hexane to give **3**. Yield: 85%. IR (KBr, cm^{−1}): ν(NH) = 3387. Anal. calcd. for C₂₂H₃₂N₂O₄ Pd: C, 53.39; H, 6.51; N, 5.66. Found: C, 53.27; H, 6.12; N, 5.61%.

4.5. Synthesis of [Pd{PhCH₂NH(Et)}₂(Cl)₂] (**4**)

To a suspension of **1** in methanol was added excess NaCl and the resulting mixture stirred for 8 h at room temperature. A green precipitate was formed which was filtered and washed with water and then air-dried to give **4**. Yield: 74%. IR (KBr, cm^{−1}): ν(NH) = 3385. Anal. calcd. for C₁₈H₂₆Cl₂N₂Pd: C, 48.28; H, 5.85; N, 6.25. Found: C, 48.44; H, 5.7; N, 6.35%.

4.6. Synthesis of [Pd₂{(C,N)-C₆H₄CH₂NH(Et)}₂(μ-Cl)₂] (**5**)

To a suspension of palladacycle **3** in methanol was added excess NaCl and the resulting mixture stirred for 12 h at room temperature. A green precipitate was formed which was filtered and washed with water and then air-dried to give **5**. Yield: 68%. IR (KBr, cm^{−1}): ν(NH) = 3233, 3194. ¹H NMR (DMSO-*d*₆, ppm): δ = 1.18 (t, 3H, CH₃, ³J_{HH} = 6.8 Hz), 2.9 (m, 2H, CH₂), 3.78 (dd, H_a, CH_aH, ²J_{HH} = 15.2 Hz, ³J_{HH} = 2.8 Hz), 4.23 (dd, H_b, CH_bH, ²J_{HH} = 14.8 Hz, ³J_{HH} = 5.2 Hz), 6.18 (br s, 1H, NH), 6.87–7.03 (m, 3H, C₆H₄), 7.63 (d, 1H, C₆H₄, ³J_{HH} = 9.2 Hz). Anal. calcd. for C₁₈H₂₄N₂Cl₂Pd₂: C, 39.15; H, 4.3; N, 5.07. Found: C, 39.17; H, 4.25; N, 5.02%.

4.7. Synthesis of $[Pd(C,N)-C_6H_4CH_2NH(t-Bu)]_2(\mu-Cl)_2$ (**6**)

To a suspension of palladacycle **4** in methanol was added excess NaCl and the resulting mixture stirred for 12 h at room temperature. A green precipitate was formed which was filtered and washed with water and then air-dried to give **6**. Yield: 64%. IR (KBr, cm^{-1}): $\nu(NH) = 3220$. 1H NMR (DMSO- d_6 , ppm): $\delta = 1.15$ (br s, 9H, t-Bu), 3.86 (m, H_a , CH_3H), 4.33 (m, H_b , CH_2H), 5.77 (br s, 1H, NH), 6.79–7 (m, 3H, C_6H_4), 7.55 (d, 1H, C_6H_4 , $^3J_{HH} = 7.6$ Hz). $^{13}C\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta = 29.8, 55.5, 57.6$ ($C_{aliphatic}$), 120.8, 124.4, 124.8, 131.9, 148.7, 153.34 ($C_{aromatic}$). Anal. calcd. for $C_{22}H_{32}N_2Cl_2Pd_2$: C, 43.44; H, 5.3; N, 4.6. Found: C, 43.23; H, 5.25; N, 4.45%.

4.8. Synthesis of $[Pd(C,N)-C_6H_4CH_2NH(t-Bu)]_2(\mu-Br)_2$ (**7**)

To a suspension of palladacycle **4** in methanol was added excess NaBr and the resulting mixture stirred for 12 h at room temperature. A green precipitate was formed which was filtered and washed with water and then air-dried to give **7**. Yield: 66%. IR (KBr, cm^{-1}): $\nu(NH) = 3203$. 1H NMR (DMSO- d_6 , ppm): $\delta = 1.16$ (br s, 9H, t-Bu), 3.88 (br s, H_a , CH_3H), 4.31 (br s, H_b , CH_2H), 5.68 (br s, 1H, NH), 6.92 (m, 3H, C_6H_4), 7.54 (br s, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta = 30.02, 57.6$ ($C_{aliphatic}$), 120.7, 124.3, 152.8 ($C_{aromatic}$). Anal. calcd. for $C_{22}H_{32}N_2Br_2Pd_2$: C, 37.9; H, 4.62; N, 4.0. Found: C, 37.85; H, 4.5; N, 4.0%.

4.9. Synthesis of $[Pd(C,N)-C_6H_4CH_2NH(Et)(phen)]BF_4$ (**8**)

$AgBF_4$ (0.035 g, 0.18 mmol) was added to a solution of complex **5** (0.05 g, 0.09 mmol) in THF (15 mL). The resulting mixture was stirred for 30 min under light protection and then filtered through a plug of $MgSO_4$ to remove $AgCl$. 1,10-Phenanthroline (0.032 g, 0.18 mmol) was added to the filtrate, and the mixture was stirred for 5 h and then filtered again through $MgSO_4$. The solvent was removed to ca. 2 mL, and *n*-hexane (15 mL) was added to precipitate **8** as a cream solid, which was collected and air-dried. Yield: 63%. IR (KBr, cm^{-1}): $\nu(NH) = 3273$. 1H NMR (DMSO- d_6 , ppm): $\delta = 1.27$ (t, 3H, CH_3 , $^3J_{HH} = 7.2$ Hz), 2.49–2.51 (m, 2H, CH_2), 3.95 (d, H_a , CH_3H , $^2J_{HH} = 16$ Hz), 4.82 (d, H_b , CH_2H , $^2J_{HH} = 14$ Hz), 6.56 (br s, 1H, C_6H_4), 6.86 (br s, 1H, NH), 7.13–7.90 (m, 3H, C_6H_4), 8.10 (br s, 1H, phen), 8.25 (t, 1H, phen, $^3J_{HH} = 7.4$ Hz), 8.29 (br s, 1H, phen), 8.66 (d, 1H, phen, $^3J_{HH} = 6$ Hz), 8.96–8.99 (m, 2H, phen), 9.14 (d, 1H, phen, $^3J_{HH} = 3.5$ Hz), 9.26 (d, 1H, phen, $^3J_{HH} = 4.8$ Hz). Anal. calcd. for $C_{21}H_{20}BF_4N_3Pd$: C, 49.68; H, 3.97; N, 8.27. Found: C, 48.85; H, 3.65; N, 8.4%.

4.10. Synthesis of $[Pd\{(C,N)-C_6H_4CH_2NH(t-Bu)\}Cl(PPh_3)]$ (**9**)

To a suspension of palladacycle **6** (0.182 g, 0.3 mmol) in dichloromethane (15 mL) was added PPh_3 (0.157 g, 0.6 mmol). The resulting solution was stirred for 8 h and then filtered through a plug of $MgSO_4$. The filtrate was concentrated to ca. 2 mL, and *n*-hexane (15 mL) was added to precipitate **9** as a pale yellow solid, which was collected and air-dried. Yield: 59%. IR (KBr, cm^{-1}): $\nu(NH) = 3186$. 1H NMR ($CDCl_3$, ppm): $\delta = 1.32$ (s, 9H, CH_3), 4.02 (d, H_a , CH_3H , $^2J_{HH} = 15$ Hz), 4.76 (d, H_b , CH_2H , $^2J_{HH} = 15$ Hz), 4.36 (br s, 1H, NH), 6.19 (d, 1H, C_6H_4 , $^3J_{HH} = 5$ Hz), 6.35 (t, 1H, C_6H_4 , $^3J_{HH} = 5$ Hz), 6.79 (t, 1H, C_6H_4 , $^3J_{HH} = 5$ Hz), 6.95 (d, 1H, Ph, $^3J_{HH} = 5$ Hz), 7.36 (m, 6H_m, PPh_3), 7.45 (m, 3H_p, PPh_3), 7.74 (m, 6H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): $\delta = 40.24$ (s, 1P, Pd– PPh_3), 41.19 (s, 1P, Pd– PPh_3). Anal. calcd. for $C_{29}H_{31}ClNPPd$: C, 61.49; H, 5.51; N, 2.47. Found: C, 61.63; H, 5.6; N, 2.56%.

4.11. Synthesis of $[Pd\{(C,N)-C_6H_4CH_2NH(t-Bu)\}Br(Me_3Py)]$ (**10**)

To a suspension of palladacycle **7** (0.348 g, 0.5 mmol) in dichloromethane (15 mL) was added Me_3Py (131 μ L, 1 mmol). The resulting solution was stirred for 8 h and then filtered through a plug

of $MgSO_4$. The filtrate was concentrated to ca. 2 mL, and *n*-hexane (15 mL) was added to precipitate **9** as a pale yellow solid, which was collected and air-dried. Yield: 62%. IR (KBr, cm^{-1}): $\nu(NH) = 3211$, $\nu(C=N) = 1621$. 1H NMR (DMSO- d_6 , ppm): $\delta = 1.16$ –1.26 (m, 9H, CH_3), 2.35 (m, 3H, CH_3), 2.83 (s, 3H, CH_3), 3.2 (s, 3H, CH_3), 3.91 (d, H_a , CH_3H , $^2J_{HH} = 16$ Hz), 4.28–4.33 (dd, H_b , CH_2H , $^2J_{HH} = 14.8$ Hz, $^3J_{HH} = 5.2$ Hz), 5.49 (d, 1H, C_6H_4 , $^3J_{HH} = 7.6$ Hz), 5.61 (br s, 1H, NH), 6.54 (t, 1H, C_6H_4), 6.79–6.94 (m, 2H, C_6H_4), 7.15 (br s, 1H, py), 7.29 (br s, 1H, py); $^{13}C\{^1H\}$ NMR (DMSO- d_6 , ppm): $\delta = 20.15, 20.29, 26.91, 27.23, 29.83, 56.31, 57.44$ ($C_{aliphatic}$), 120.2, 121.05, 123.6, 123.8, 124.3, 129.4, 152.1, 157.6, 158.2 ($C_{aromatic}$). Anal. calcd. for $C_{19}H_{27}N_2BrPd$: C, 48.5; H, 5.79; N, 5.9. Found: C, 48.8; H, 5.65; N, 5.72%.

4.12. X-ray structure determinations

X-ray diffraction data for **3**, **4**, **8** and **9** were collected at 100 K with the use of Agilent SuperNova single crystal diffractometer and corrected for absorption using a multifaceted crystal model based on expressions derived by Clark & Reid [23]. Data for **2** and **10** were collected at ambient temperature using a Bruker APEX-II CCD diffractometer and corrected for absorption using the SADABS program [24]. Graphite monochromatized Mo ($K\alpha$) radiation was used for all data collections. The structures were solved by direct methods using the SHELXS97 (for **3**, **4**, **8** and **9**) [25] or SIR97 (for **2** and **10**) [26] program and refined with the use of the SHELXL97 program [25]. Hydrogen atoms were positioned geometrically and refined as riding on their parent atoms during the refinement. The amine H atom of **2** and **10** were located in a difference Fourier map and refined freely.

Acknowledgments

We are grateful for the financial support from the Department of Chemistry, Isfahan University of Technology (IUT). We gratefully thank the Iran National Science Foundation (INSF) for financial support.

Appendix A. Supplementary material

CCDC 905807–12 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2012.12.032>.

References

- [1] I. Omae, Coord. Chem. Rev. 248 (2004) 995–1023.
- [2] I.P. Beletskaya, A.V. Cheprakov, J. Organomet. Chem. 689 (2004) 4055–4082.
- [3] A.C. Cope, E.C. Friedrich, J. Am. Chem. Soc. 90 (1968) 909–913.
- [4] Y. Fuchita, K. Yoshinaga, T. Hanaki, H. Kawano, J. Kinoshita-Nagaoka, J. Organomet. Chem. 580 (1999) 273–281.
- [5] K. Selvakumar, S. Vancheesan, Polyhedron 16 (1997) 2405–2411.
- [6] S.A. Kurzev, G.M. Kazanov, A.D. Ryabov, Inorg. Chim. Acta 340 (2002) 192–196.
- [7] Y. Fuchita, H. Tsuchiya, A. Miyafuji, Inorg. Chim. Acta 233 (1995) 91–96.
- [8] Y. Fuchita, H. Tsuchiya, Inorg. Chim. Acta 209 (1993) 229–230.
- [9] J. Vicente, I. Saura-Llamas, J. Turpón, M.C. Ramírez De Arellano, P.G. Jones, Organometallics 18 (1999) 2683–2693.
- [10] K. Karami, M.M. Salah, Appl. Organomet. Chem. 24 (2010) 828–832.
- [11] K. Karami, C. Rizzoli, N. Rahimi, Transit. Met. Chem. 36 (2011) 841–846.
- [12] K. Karami, N. Rahimi, M. Bahrani Shehni, Tetrahedron Lett. 53 (2012) 2428–2431.
- [13] J. Vicente, I. Saura-Llamas, J. Cuadrado, M.C. Ramírez de Arellano, Organometallics 22 (2003) 5513–5517.
- [14] L. Cattalini, M. Martelli, J. Am. Chem. Soc. 91 (1969) 312–316.
- [15] V.K. Jain, L. Jain, Coord. Chem. Rev. 249 (2005) 3075–3197.
- [16] R.E. Rulke, J.G.P. Delis, A.M. Groot, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, K. Goubitz, H.J. Schenk, J. Organomet. Chem. 508 (1996) 109–120.
- [17] J.G.P. Delis, P.G. Aubel, K. Vrieze, P.W.N.M. van Leeuwen, N. Veldman, A.L. Spek, Organometallics 16 (1997) 4150–4160.

- [18] R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, P.N. Horton, M.B. Hursthouse, M.E. Light, *Organometallics* 22 (2003) 987–999.
- [19] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, *Eur. J. Inorg. Chem.* (2002) 2389–2401.
- [20] J. Albert, J. Granell, J. Zafra, M. Font-Bardia, X. Solans, *J. Organomet. Chem.* 690 (2005) 422–429.
- [21] J.M. Chitanda, J. Wilson Quail, S.R. Foley, *J. Organomet. Chem.* 694 (2009) 1542–1548.
- [22] R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, New Jersey, 2005.
- [23] R.C. Clark, J.S. Reid, *Acta Crystallogr. A* 51 (1995) 887–897.
- [24] G.M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1996.
- [25] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112–122.
- [26] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 32 (1999) 115–119.