Palladium complexes of a new type of N-heterocyclic carbene ligand derived from a tricyclic triazolooxazine framework

MANOJ KUMAR GANGWAR, ALOK CH KALITA and PRASENJIT GHOSH*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India
e-mail: pghosh@chem.iitb.ac.in

MS received 9 April 2014; revised 22 April 2014; accepted 14 May 2014

Abstract. A new type of tricyclic triazolooxazine derived N-heterocyclic carbene precursors were developed by the alkylation reaction of a tricyclic triazolooxazine framework. In particular, the reaction of 5a,6,7,8,9,9a-hexahydro-4*H*-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazine with methyl iodide and ethyl iodide yielded the tricyclic triazolooxazine derived N-heterocyclic carbene precursors, (1–2)**a**, in 67–84% yield. The tricyclic triazolooxazinium iodide salts, (1–2)**a**, underwent metallation in a straight forward manner upon treatment with PdCl₂ in the presence of K₂CO₃ in pyridine to give the *trans*-{3-(*R*)-5a,6,7,8,9,9a-hexahydro-4*H*-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-ylidene} PdI₂(pyridine) [R = Me (**1b**), Et (**2b**)] complexes in 23–25% yield. The new tricyclic triazolooxazine derived N-heterocyclic carbene moiety, as stabilized upon binding to palladium in the (1–2)**b** complexes, was structurally characterized by the X-ray single crystal diffraction studies.

Keywords. Palladium; tricyclic triazolooxazine derived N-heterocyclic carbene (NHC); PEPPSI.

1. Introduction

The unprecedented success of the imidazole-based N-heterocyclic carbenes as wonder ligands in homogeneous catalysis has generated immense interest in other variants of these stable singlet carbene ligands¹ as part of a larger effort on gauging their true potential in the area.² Consequently, large number of structural motifs of varying types have been developed of these carbene ligands that extend much beyond the more conventional imidazole based saturated and unsaturated five-membered carbenes to pyrazole derived carbenes, six-, seven-, and eight-membered NHCs, acyclic diaminocarbenes (ADCs), abnormal mesoionic NNCs, to name a few. All these carbene ligands showcase some very elegant and innovative work in the dual realms of synthesis and homogeneous catalysis. These developments have largely advanced the fields of asymmetric catalysis,¹¹ various types of polymerization¹² reactions, organocatalysis,¹³ and the countless methodology development reactions of relevance to the organic synthesis¹⁴ extending all the way to total synthesis.¹⁵

One of our longstanding objective remains to identify and understand the key attributes of the N-heterocyclic carbenes responsible for their phenomenal success in homogeneous catalysis.¹⁶ In this regard, we have looked into various types of N-heterocyclic carbene ligand

frameworks of the 5-membered imidazole¹⁷ and the triazole¹⁸ rings, a 6-membered¹⁹ saturated cyclic ring and the imidazo[1,2-*a*]pyridine²⁰ scaffolds for a host of different transformations like, the C–C cross-coupling reaction, the base-free Michael addition reaction, the C–N bond forming alkene and alkyne hydroamination reactions and the ring-opening polymerization of the L-lactides. Proceeding further along the line, we set out to look into the other new motifs of the N-heterocyclic carbene ligands. In particular, we became interested in the N-fused tricyclic ring derived carbene ligands having chiral centres with restricted rotation as these are expected to significantly facilitate more asymmetric induction during the catalysis over the analogous carbene ligands having free-rotation of their chiral ancillary. To start with, we decided to synthesize the racemic versions of these tricyclic triazolooxazine derived N-heterocyclic carbene ligands with the intent of overcoming the synthetic challenge and for establishing the preparative protocol before taking up the synthesis of their asymmetric counterparts.

Herein, we report a new tricyclic triazolooxazine derived N-heterocyclic carbene ligand stabilized in its (NHC)PdI₂(pyridine) type palladium complexes, and the structural characterization of which provide valuable insights into the binding preference of this new ligand.

*For correspondence

2. Experimental

2.1 General procedures

All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Cyclohexene oxide and propargyl bromide were purchased from Sigma Aldrich Chemicals and used without any further purification. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), doublet of triplets (dt), triplet of triplets (tt), multiplet (m). The 5a,6,7,8,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazine²¹ was synthesized by modification of a procedure reported in literature. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-ToF spectrometer. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data were collected on a Rigaku Hg 724+ diffractometer.

2.2 Synthesis of 3-methyl-5a,6,7,8,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene} PdI₂(pyridine) (**1a**)

A mixture of 5a,6,7,8,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazine (4.67 g, 26.0 mmol) and methyl iodide (18.5 g, 131 mmol) was refluxed overnight in acetonitrile (*ca.* 100 mL), after which, the solvent was removed under vacuum. The yellow solid thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with methanol/chloroform (*v/v* 1:9) to give the product as a light yellow solid **1a** (6.99 g, 84%). ^1H NMR (CDCl_3 , 500 MHz, 25°C): δ 9.24 (s, 1H, C_2HN_3 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 5.33 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 5.22 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 4.51 (s, 3H, CH_3), 4.26–4.21 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 3.98–3.93 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 2.79–2.76 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 2.22–2.20 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 1.99–1.84 (m, 3H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 1.61–1.48 (m, 3H, C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, 25°C): δ 137.1 (C_2HN_3 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 128.0 (C_2HN_3 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 77.0 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 63.4 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 61.6 (OCH_2 of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 41.2 (CH_3), 29.8 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 27.0 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 23.2 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$), 23.0 (C_6H_{10} of $\text{C}_9\text{H}_{13}\text{N}_3\text{O}$). IR data (cm^{-1}) KBr pellet: 3108 (w), 2997 (w), 2955

(m), 2943 (m), 2897 (w), 2868 (w), 1577 (w), 1447 (m), 1436 (m), 1378 (w), 1336 (m), 1299 (w), 1276 (w), 1172 (m), 1093 (s), 1087 (s), 1059 (m), 1027 (m), 950 (w), 942 (w), 847 (w), 829 (m), 806 (m), 755 (w), 626 (w). HRMS (ES): m/z 194.1288, $(\text{M})^+$, Calcd. 194.1288. Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{IN}_3\text{O}$: C, 37.40; H, 5.02; N, 13.08. Found: C, 37.20; H, 4.63; N, 13.07.

2.3 Synthesis of trans-3-methyl-5a,6,7,8,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene} PdI₂(pyridine) (**1b**)

A mixture of 3-methyl-5a,6,7,8,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene} PdI₂(pyridine) (0.588 g, 1.82 mmol), PdCl₂ (0.325 g, 1.82 mmol), K₂CO₃ (2.02 g, 14.7 mmol) and NaI (1.37 g, 9.14 mmol) was refluxed in pyridine (*ca.* 7 mL) for 16 hours. The reaction mixture was then cooled to room temperature, diluted with CHCl₃ (*ca.* 200 mL) and subsequently washed with saturated aqueous CuSO₄ solution (*ca.* 3 × 50 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under vacuum to give a sticky, brown residue. The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with methanol/chloroform (*v/v* 1:9) mixture to give the product as a yellow solid **1b** (0.295 g, 25%). The product was crystallized from CHCl₃. ^1H NMR (CDCl_3 , 500 MHz, 25°C): 9.03–9.01 (m, 2H, NC_5H_5), 7.73–7.70 (m, 1H, NC_5H_5), 7.32–7.30 (m, 2H, NC_5H_5), 5.32 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 5.02 (d, 1H, $^2J_{\text{HH}} = 16$ Hz, OCH_2 of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 4.36 (s, 3H, CH_3), 3.93–3.89 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 3.55–3.50 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 2.69–2.67 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 2.21–2.18 (m, 1H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 1.93 (br, 2H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 1.57–1.41 (m, 4H, C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz, 25°C): δ 154.0 (NC_5H_5), 138.0 (NC_5H_5), 137.6 (C_2N_3 of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 129.0 (C_2N_3 of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 124.5 (NC_5H_5), 76.9 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 64.0 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 62.3 (OCH_2 of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 43.22 (CH_3), 30.5 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 29.8 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 27.4 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$), 23.8 (C_6H_{10} of $\text{C}_9\text{H}_{12}\text{N}_3\text{O}$). IR data (cm^{-1}) KBr pellet: 2923 (m), 2859 (m), 1603 (m), 1525 (w), 1484 (w), 1446 (s), 1370 (w), 1300 (m), 1265 (m), 1207 (w), 1144 (w), 1088 (s), 1066 (m), 1046 (w), 1024 (w), 904 (w), 877 (w), 842 (m), 761 (m), 696 (m), 670 (w). HRMS (ES): m/z 654.8688, $[\text{M}+\text{Na}]^+$, Calcd. 654.8659. Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{I}_2\text{N}_4\text{OPd}$: C, 28.48; H, 3.19; N, 8.86. Found: C, 29.26; H, 3.18; N, 7.97.

2.4 Synthesis of 3-ethyl-5a,6,7,8,9,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene (2a)

A mixture of 5a,6,7,8,9,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazine (2.13 g, 11.9 mmol) and ethyl iodide (9.30 g, 59.6 mmol) was refluxed overnight in acetonitrile (*ca.* 100 mL), after which, the solvent was removed under vacuum. The yellow solid thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with methanol/chloroform (*v/v* 1:9) to give the product a light yellow solid **2a** (2.67 g, 67%). ¹H NMR (CDCl₃, 500 MHz, 25°C): δ 9.22 (s, 1H, C₂H_N of C₉H₁₃N₃O), 5.28 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₉H₁₃N₃O), 5.18 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₉H₁₃N₃O), 4.82–4.73 (m, 2H, CH₂CH₃), 4.19–4.14 (m, 1H, C₆H₁₀ of C₉H₁₃N₃O), 3.91 (dt, 1H, ²J_{HH} = 10 Hz, ³J_{HH} = 4 Hz, C₆H₁₀ of C₉H₁₃N₃O), 2.75–2.72 (m, 1H, C₆H₁₀ of C₉H₁₃N₃O), 2.18–2.16 (m, 1H, C₆H₁₀ of C₉H₁₃N₃O), 1.99–1.79 (m, 3H, C₆H₁₀ of C₉H₁₃N₃O), 1.68 (t, 3H, ³J_{HH} = 8 Hz, CH₂CH₃), 1.56–1.47 (m, 3H, C₆H₁₀ of C₉H₁₃N₃O). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25°C): δ 137.3 (C₂HN₃ of C₉H₁₃N₃O), 127.3 (C₂HN₃ of C₉H₁₃N₃O), 77.0 (C₆H₁₀ of C₉H₁₃N₃O), 63.7 (C₆H₁₀ of C₉H₁₃N₃O), 61.9 (OCH₂ of C₉H₁₃N₃O), 50.1 (CH₂CH₃), 30.0 (C₆H₁₀ of C₉H₁₃N₃O), 27.2 (C₆H₁₀ of C₉H₁₃N₃O), 23.5 (C₆H₁₀ of C₉H₁₃N₃O), 23.2 (C₆H₁₀ of C₉H₁₃N₃O), 14.8 (CH₂CH₃). IR data (cm⁻¹) KBr pellet: 3155 (w), 3118 (w), 2975(w), 2947 (s), 2936 (s), 2863 (m), 1629 (w), 1572 (w), 1450 (m), 1383 (w), 1338 (m), 1299 (w), 1245 (w), 1160 (m), 1146 (m), 1136 (m), 1093 (s), 1082 (s), 1028 (m), 940 (w), 874 (w), 846 (w), 817 (m), 786 (w), 751 (w), 656 (w). HRMS (ES): (M)⁺, *m/z* 208.1445, Calcd. 208.1444. Anal. Calcd. for C₁₁H₁₈N₃O: C, 39.42; H, 5.41; N, 12.54. Found: C, 39.22; H, 5.02; N, 12.45.

2.5 Synthesis of trans{ 3-ethyl-5a,6,7,8,9,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene} PdI₂(pyridine) (2b)

A mixture of 3-ethyl-5a,6,7,8,9,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene (0.500 g, 1.49 mmol), PdCl₂ (0.264 g, 1.49 mmol), K₂CO₃ (1.64 g, 11.9 mmol) and NaI (1.11 g, 7.46 mmol) was refluxed in pyridine (*ca.* 5 mL) for 16 hours. The reaction mixture was then cooled to room temperature, diluted with CHCl₃ (*ca.* 100 mL) and subsequently washed with saturated aqueous CuSO₄ solution (*ca.* 3 × 50 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under vacuum to give a sticky, brown residue.

The residue thus obtained was further purified by column chromatography using silica gel as a stationary phase and eluted with methanol/chloroform (*v/v* 1:9) mixture to give the product as a yellow solid **2b** (0.220 g, 23%). The product was crystallized from CH₃CN. ¹H NMR (CDCl₃, 500 MHz, 25°C): 9.02–9.01 (m, 2H, NC₅H₅), 7.73–7.70 (m, 2H, NC₅H₅), 7.32–7.29 (m, 1H, NC₅H₅), δ 5.33 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₉H₁₂N₃O), 5.02 (d, 1H, ²J_{HH} = 16 Hz, OCH₂ of C₉H₁₂N₃O), 4.87–4.76 (m, 2H, CH₂CH₃), 3.95–3.90 (m, 1H, C₆H₁₀ of C₉H₁₂N₃O), 3.56–3.53 (m, 1H, C₆H₁₀ of C₉H₁₂N₃O), 2.71–2.68 (m, 1H, C₆H₁₀ of C₉H₁₂N₃O), 2.21–2.19 (m, 1H, C₆H₁₀ of C₉H₁₂N₃O), 1.96–1.91 (m, 2H, C₆H₁₀ of C₉H₁₂N₃O), 1.74 (t, 3H, ³J_{HH} = 8 Hz, CH₂CH₃), 1.61–1.41 (m, 4H, C₆H₁₀ of C₉H₁₂N₃O). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25°C): δ 153.8 (NC₅H₅), 137.6 (NC₅H₅), 137.4 (C₂N₃ of C₉H₁₂N₃O), 127.4 (C₂N₃ of C₉H₁₂N₃O), 124.3 (NC₅H₅), 76.8 (C₆H₁₀ of C₉H₁₂N₃O), 64.0 (C₆H₁₀ of C₉H₁₂N₃O), 62.2 (OCH₂ of C₉H₁₂N₃O), 51.3 (CH₂), 30.3 (C₆H₁₀ of C₉H₁₂N₃O), 27.2 (C₆H₁₀ of C₉H₁₂N₃O), 23.7 (C₆H₁₀ of C₉H₁₂N₃O), 23.6 (C₆H₁₀ of C₉H₁₂N₃O), 14.7 (CH₃). IR data (cm⁻¹) KBr pellet: 2937 (m), 2861 (m), 1603 (m), 1483 (w), 1445 (s), 1370 (w), 1299 (m), 1238 (w), 1146 (w), 1090 (s), 1066 (m), 1026 (m), 938 (w), 877 (w), 831 (w), 757 (m), 691 (m). HRMS (ES): *m/z* 668.8818, [M+Na]⁺, Calcd. 668.8816. Anal. Calcd. for C₁₆H₂₂I₂N₄OPd: C, 29.72; H, 3.43; N, 8.66. Found: C, 29.94; H, 3.04; N, 8.42.

3. Results and Discussions

A new type of the tricyclic triazolooxazine derived N-heterocyclic carbene namely, 3-(R)-5a,6,7,8,9,9a-hexahydro-4H-benzo[b][1,2,3]triazolo[1,5-d][1,4]oxazin-4-ylidene [R = Me, Et], was developed to assess its potential as a new ligand in the backdrop of their largely successful imidazole derived counterparts in homogeneous catalysis. The tricyclic triazolooxazine derived N-heterocyclic carbene precursors (**1–2a**), were

Figure 1. Pd complexes of the tricyclic triazolooxazine derived N-heterocyclic carbene (NHC) ligands.

obtained from the reaction of 5a,6,7,8,9,9a-hexahydro-4*H*-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazine with the methyl and ethyl iodides in refluxing CH₃CN in 67–84 % yield. The formation of the carbene precursors (**1–2**)**a** were evident from the presence of the pro-carbene centre proton resonance corresponding to the 4-position of the tricyclic triazolooxazine ring at 9.24 ppm (**1a**) and 9.22 ppm (**2a**) in the ¹H NMR spectrum and the pro-carbene centre carbon resonance in the 127.9 ppm (**1a**) and 127.2 ppm (**2a**) in the ¹³C NMR spectrum. The HRMS spectrum of the 3-(*R*)-tricyclic triazolooxazinium iodide salts (**1–2**)**a** exhibited *m/z* peaks at 194.1288 (**1a**) and 208.1444 (**2a**) consistent with the respective calculated values of 194.1293 (*m/z*) and 208.1450 (*m/z*).

The stabilization of the new tricyclic triazolooxazine derived N-heterocyclic carbene was achieved in its palladium complexes, (**1–2**)**b** that were obtained by treating 3-(*R*)-tricyclic triazolooxazinium iodide salts (**1–2**)**a** with PdCl₂ in presence of K₂CO₃ in refluxing pyridine in 23–25 % yield. Consistent with the presence of a metal bound carbene moiety, the palladium complexes (**1–2**)**b**, exhibited an expected Pd–C_{carbene} resonance at the 129.0 ppm (**1b**) and 127.4 ppm (**2b**) in the ¹³C NMR spectrum and an absence of a peak in the 9.22–9.24 ppm region of the ¹H NMR spectrum, where the pro-carbene centre proton resonance of the 4-position of the tricyclic triazolooxazine ring of the starting material (**1–2**)**a** appeared.

The final confirmation, however, came from the molecular structure determination of the palladium

(**1–2**)**b** complexes, that showed that the tricyclic triazolooxazine derived N-heterocyclic carbene moiety was indeed bound to a square planar palladium centre *trans* to a pyridine moiety while the remaining two sites around the metal centre were occupied by two iodide atoms (figures 1–3, table 1 and scheme 1). Consistent with a square planar geometry, all of the four angles at palladium namely, the ∠C_{carbene}–Pd–I and the ∠I–Pd–N_{pyridine}, and their respective complementary angles are close to 90 degrees. The Pd–I distances were observed to be of 2.6187(17) Å and 2.5904(17) Å in **1b** and of 2.6123(10) Å and 2.6031(10) Å in **2b**.

Of foremost importance, is the Pd–C_{carbene} distance [1.989(14) Å (**1b**); 1.961(6) Å (**2b**)], which are shorter than the sum of the individual covalent radii of Pd and C (2.055 Å)²² but fall well within the range observed in other related representative complexes like the triazole derived *trans*-[1-ethyl-3-methyl-4-phenyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [1.9601(16) Å],²³ *trans*-[1,4-di-*n*-butyl-3-methyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [1.9650(13) Å],²³ *trans*-[1-mesityl-3-methyl-4-phenyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [1.957(3) Å],²³ *trans*-[1,4-bis(2,6-diisopropylphenyl)-3-methyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [1.965(2) Å],²⁴ [*trans*-[4-benzyl-1-*i*-propyl-1,2,4-triazol-5-ylidene]PdBr₂(pyridine) [1.950(9) Å]¹⁸ and *trans*-[4-benzyl-1-(*t*-butylaminocarbonylmethyl)-1,2,4-triazol-5-ylidene]PdBr₂(pyridine) [1.946(3) Å]¹⁸ complexes and the imidazole derived *trans*-[1-(benzyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]PdCl₂(pyridine) [1.957(3) Å],²⁵ and [*trans*-[1-(2-hydroxy-cyclohexyl)-

Figure 2. ORTEP of **1b** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(2)–C(16) 1.989(14), Pd(2)–N(8) 2.090(11), Pd(2)–I(3) 2.6187(17), Pd(2)–I(4) 2.5904(17), C(16)–Pd(2)–N(8) 177.9(6), C(16)–Pd(2)–I(3) 89.6(4), N(8)–Pd(2)–I(3) 92.3(3), C(16)–Pd(2)–I(4) 86.1(4), N(8)–Pd(2)–I(4) 92.0(3), I(4)–Pd(2)–I(3) 175.15(6).

Figure 3. ORTEP of **2b** with thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.961(6), Pd(1)–N(4) 2.096(5), Pd(1)–I(1) 2.6123(10), Pd(1)–I(2) 2.6031(10), C(1)–Pd(1)–N(4) 177.7(2), C(1)–Pd(1)–I(1) 88.58(16), N(4)–Pd(1)–I(1) 92.37(12), C(1)–Pd(1)–I(2) 88.38(16), N(4)–Pd(1)–I(2) 90.17(12), I(2)–Pd(1)–I(1) 176.71(2).

3-(benzyl)imidazol-2-ylidene]PdCl₂(pyridine) [1.967(4) Å],²⁵ complexes.

The Pd–N_{pyridine} distance [2.090(11) (Å) (**1b**); 2.096(5) (Å) (**2b**)] are longer than the sum of the individual covalent radii of Pd and N (1.983 Å)²² but are comparable to the other related complexes like the triazole derived *trans*-[1-ethyl-3-methyl-4-phenyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [2.1105(13) Å],²³ *trans*-[1,4-di-*n*-butyl-3-methyltriazol-5-ylidene]PdCl₂

(3-chloropyridine) [2.1192(11) Å],²³ *trans*-[1-mesityl-3-methyl-4-phenyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [2.129(3) Å],²³ *trans*-[1,4-bis(2,6-diisopropylphenyl)-3-methyltriazol-5-ylidene]PdCl₂(3-chloropyridine) [2.089(2) Å],²⁴ *trans*-[4-benzyl-1-*i*-propyl-1,2,4-triazol-5-ylidene]PdBr₂(pyridine) [2.092(8) Å]¹⁸ and *trans*-[4-benzyl-1-(*t*-butylaminocarbonylmethyl)-1,2,4-triazol-5-ylidene]PdBr₂(pyridine) [2.100(3) Å]¹⁸ complexes and the imidazole derived *trans*-[1-(benzyl)-3-

Table 1. X-ray crystallographic data for **1b** and **2b**.

Compound	1b	2b
Lattice	Triclinic	Monoclinic
Formula	C ₁₅ H ₂₀ I ₂ N ₄ OPd	C ₁₆ H ₂₂ I ₂ N ₄ OPd
Formula weight	632.55	646.58
Space group	<i>P</i> -1	<i>P</i> 21/ <i>c</i>
<i>a</i> /Å	10.087(5)	10.265(5)
<i>b</i> /Å	12.898(7)	13.121(6)
<i>c</i> /Å	15.835(7)	15.757(8)
α /°	87.335(16)	90
β /°	74.701(14)	104.239(8)
γ /°	83.549(16)	90
<i>V</i> /Å ³	1974.3(17)	2057.1(17)
<i>Z</i>	4	4
Temperature (K)	100(2)	100(2)
Radiation (λ , Å)	0.7107	0.7107
ρ (calcd.), g c ⁻³	2.128	2.088
μ (Mo α), m ⁻¹	4.076	3.914
θ max, deg.	29.21	25.00
No. of data	10547	3608
No. of parameters	420	217
<i>R</i> ₁	0.0878	0.0384
<i>wR</i> ₂	0.2128	0.0720
GOF	1.116	1.161

Scheme 1. Synthesis of Pd-NHC complexes (**1–2b**).

(*N*-*t*-butylacetamido)imidazol-2-ylidene]PdCl₂(pyridine) [2.089(3) Å],²⁵ and *trans*-[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]PdCl₂(pyridine) [2.096(3) Å]²⁵ complexes.

Overall, though the tricyclic triazolooxazine derived N-heterocyclic carbene ligand exhibited analogous binding orientation to palladium similar to the other commonly observed imidazole and triazole derived N-heterocyclic carbene ligands in the (NHC)PdI₂(pyridine) type complexes, their steric and electronic influences on the metal remains to be uncovered and would be the subject of future publications from the group.

4. Conclusion

A new type of tricyclic triazolooxazine derived N-heterocyclic carbene ligand precursors namely, 3-(R)-5a,6,7,8,9,9a-hexahydro-4*H*-benzo[*b*] [1,2,3]triazolo[1,5-*d*][1,4]oxazinium iodide, (**1–2a**), was conveniently synthesized by the alkylation reaction of a tricyclic triazolooxazine framework. The new tricyclic triazolooxazine derived N-heterocyclic carbene moiety was stabilized in its palladium complexes, (**1–2b**), which were obtained upon metallation of the tricyclic triazolooxazinium iodide salts, (**1–2a**), with PdCl₂ in presence of K₂CO₃ in pyridine.

Supplementary Information

CCDC-983594 (for **1b**), CCDC-978994 (for **2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Department of Science and Technology (Grant No: SR/S1/IC-50/2011), New Delhi, for financial support of this research. We thank Professor R. Murugavel for the use of his Single Crystal X-ray Diffraction Facility established through a DAE-SRC

Outstanding Investigator Award along with the Single Crystal X-ray Diffraction Facility, Department of Chemistry IIT Bombay, India, for the crystallographic characterization data. MKG thanks CSIR, New Delhi for research fellowship.

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