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Chloropalladated tetranuclear and copper(I) complexes of propargylamines [RC≡CCH$_2$NC$_4$H$_8$NCH$_2$C≡CR]

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ABSTRACT

The reactions of propargylamines *1,4*-bis(3-phenylprop-2-yn-1-yl)piperazine (**1**) and *1,4*-bis(3-(trimethylsilyl)prop-2-yn-1-yl)piperazine (**2**) with $PdCl_2$ and CuI is described. *1,4*-Bis(3-phenylprop-2-yn-1-yl) piperazine reacts with one equivalent of $PdCl_2$ to afford κ^2-*N,N*-coordinated complexes [$PdCl_2${Me_3SiC≡$CCH_2NC_4H_8NCH_2$C≡CSiMe_3-κ^2-*N,N*] (**3**) and [$PdCl_2${Me_3SiC≡$CCH_2NC_4H_8NCH_2$C≡CSiMe_3}-κ^2-*N,N*] (**4**). The reactions of **1** and **2** with two equivalents of $PdCl_2$ yielded rare chloropalladated tetranuclear complexes [$Pd_4(\mu$-Cl)$_4$(PhC=C(Cl)$CH_2NC_4H_8NCH_2$(Cl)C=CPh)$_2$] (**5**) and [$Pd_4(\mu$-Cl)$_4$(Me_3SiC=C(Cl) $CH_2NC_4H_8NCH_2$(Cl)C=CSiMe_3)$_2$] (**6**), respectively, resulting from the *trans* nucleophilic addition of chloride ion onto the electrophilic C≡C bond. The reactions of **1** and **2** with two equivalents of CuI produced 2-D coordination polymers [{$Cu_2(\mu$-I)}$_2$(PhC≡C–$CH_2NC_4H_8NCH_2$C≡CPh)]$_n$ (**7**) and [{$Cu_2(\mu$-I)}$_2$(Me_3SiC≡$CCH_2NC_4H_8NCH_2$C≡CSiMe_3)]$_n$ (**8**), respectively. Similar reactions in 1:1 M ratios produced dimeric complexes [$Cu_2(\mu$-I)$_2$(PhC≡$CCH_2NC_4H_8NCH_2$C≡CPh)$_2$] (**9**) and [$Cu_2(\mu$-I)$_2$(Me_3SiC≡$CCH_2NC_4H_8NCH_2$C≡CSiMe_3)$_2$] (**10**), respectively. The structures of compounds **3**, **5** and **7** have been established by single crystal X-ray analysis.

1. Introduction

Alkynes are very important starting materials in carbon–carbon cross coupling [1–5], Diels-Alder cyclization reaction [6–8], metal-organic frameworks (MOF's) [9], polymerization reactions [10–14], and also in the preparation of several pincer ligands as substrates [15–18]. Alkynes with functionalities such as amine, ether and thioether are excellent precursors in organic and organometallic synthesis (Chart 1) [2,15]. The propargylamines are very useful reagents for trapping organometallic intermediates such as chloropalladates, carba-palladates and other organometallic species [16,19–21]. The chloropalladation reaction includes the activation of alkynes, alkenes, cyclopropanes and their conversion into alkenes, substituted chloro-products and breakage of cyclopropane ring by transferring the chloride ion (Chart 1, A-E) [9,22–24]. The chloropalladation reactions of active cyclopropane and cyclopropene have also been extensively studied [1,22,23,25–33]. Chloropalladation is one of the key reactions in pharmaceutical industries to produce many drug molecules [34,35]. Dupont and co-workers have reported a series of *cis* and *trans* dinuclear chloropalladated complexes of propargyl amines and thioethers which are found to be key intermediates in anti-hydrochlorination of unactivated alkynes [16,20,21]. However, to the best of our knowledge, there are no reports on tetranuclear complex formation in chloropalladation reactions. The propagylamines *1,4*-bis(3-phenylprop-2-yn-1-yl)piperazine (**1**) and *1,4*-bis(3-(trimethylsilyl) prop-2-yn-1-yl)piperazine (**2**) having two propargyl groups as side arms are suitable candidates for the formation of tetranuclear chloropalladated products. Similar coordination behavior is anticipated in the reactions of nitrogen donor ligands with copper(I) halides [36,37]. Nitrogen donor ligands often form 2-D or 3-D polymers [36–39] and many of them find applications in catalysis [36,40–42], photoluminescence [43] or fluorescence studies [44]. It is anticipated that the propagylamines **1** and **2** having acetylene groups can form interesting complexes. In this context, we sought to look into the reactions of propargylamines with palladium(II) as well as copper(I) salts. The details are described in this communication.

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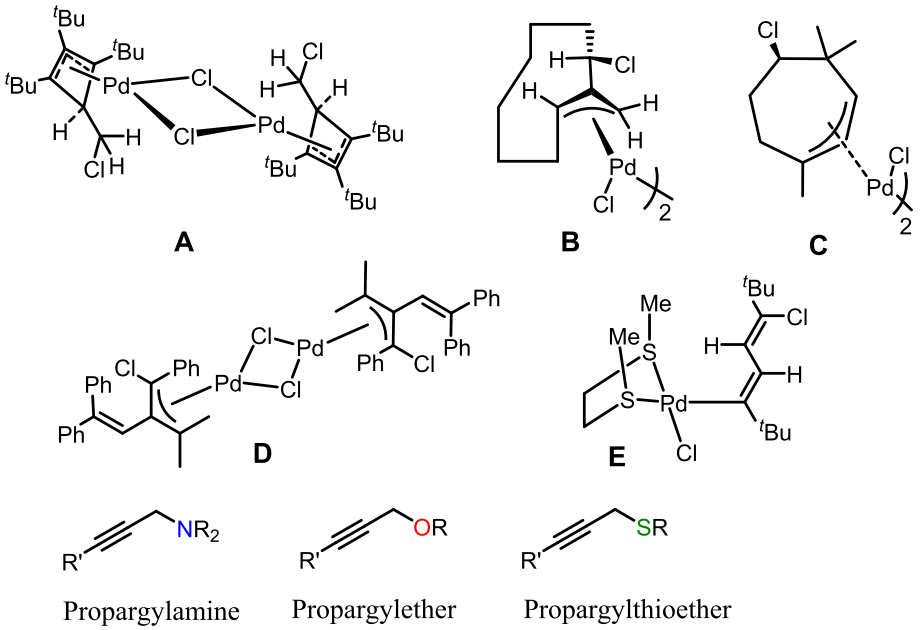


Chart 1. Some chloropalladated products and alkynes with various functionalities.

2. Experimental section

2.1. General procedures

All the reactions were performed under aerobic conditions. All the solvents were purified by conventional procedures and distilled prior to use. The metal precursors $PdCl_2$ and CuI were purchased from Aldrich chemicals and used as received. Compounds **1** and **2** were prepared according to published procedures [45].

2.2. Instrumentation

The ^1H and $^{13}C\{^1H\}$ NMR (δ in ppm) spectra were obtained from either Bruker Avance-400 MHz or Bruker Avance-500 MHz spectrometer. The spectra were recorded in $CDCl_3$ solution with $CDCl_3$ (or DMSO-d_6) as an internal lock; TMS was used as internal standard for ^1H and $^{13}C\{^1H\}$ NMR. Positive values indicate downfield shifts. Mass spectra were recorded on BRUKER mass spectrometer using Electron-spray ionization mass spectrometry (ESI-MS) method. The powder X-ray diffraction (PXRD) was carried out on EMPYREAN, Malvern Panalytical diffractometer with Cu Kα radiation ($\lambda = 1.54184$ Å). Data were collected in rectangular sample holder of dimension of Vol. 0.6 cm^3 i.e. l = 2, b = 1.5, h = 0.2 cm at 298 K using a scan range (2θ/deg.) 5–100. Elemental analyses was performed using Thermo Quest CE instrumentFLASH EA 1112 series. Melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected.

2.3. X-ray crystallography

A crystal of each of the compounds in the present work suitable for single-crystal X-ray diffraction studies was mounted in a cryoloop with a drop of paratone oil and placed in the cold nitrogen stream of the kryoflex attachment of the Rigaku Saturn 724+ (4 × 4 bin mode) diffractometer for compounds mentioned in crystallographic data table. Data were collected at 150 K as shown in crystallographic data (Table 1), using graphite-monochromated Mo Kα radiation ($\lambda\alpha = 0.71073$ Å) with the ω-scan technique. The data were collected and reduced using CrystalClear-SM Expert 2.0 r7 software. The structures were solved using Olex2 [46] with the ShelXT [47] structure solution program using intrinsic phasing and refined with the ShelXL [48] refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. In case of **5**, the structure was refined as a non-merohedral twin. There is no twin law as such but the twinning is related to a 180 deg rotation. Component 2 rotated by 179.3018\% around [-0.33 -0.49 0.81] (reciprocal) or [-0.57 -0.58 0.58] (direct). As far as the omitted reflections are concerned the reflections with error/esd more than 10 and the reflections obscured by the beamstop were excluded in order to avoid problems related to the better refinement of the data. Crystallographic data (including structures

Table 1
Crystallographic information for compounds **3**, **5**, and **7**.

	3	5	7
Formula	$C_{22}H_{22}Cl_2N_2Pd$	$C_{44}H_{40}Cl_8N_4Pd_4$ 2(CH_2Cl_2)	$C_{11}H_{11}CuIN$
Formula Weight	491.71	1503.85	347.65
Crystal System	Orthorhombic	Triclinic	monoclinic
Space group	*Pbcn*	*P-1*	$P2_1/c$
a [Å]	28.824(3)	9.2998(5)	10.2784(6)
b [Å]	7.7381(6)	11.1193(6)	7.0389(4)
c [Å]	9.4523(9)	12.6899(8)	15.4443(8)
α [°]	90	94.677(5)	90
β [°]	90	96.225(5)	98.372(5)
γ [°]	90	102.646(4)	90
V [$Å^3$]	2108.3(3)	1265.32(13)	1105.46(11)
Z	4	1	4
ρ_{calc} [gcm^{-3}]	1.549	1.953	2.089
μ (Mo-K_α) [mm^{-1}]	1.143	2.049	4.727
F(000)	992	736	664
T (K)	150	150	150
2θ range, [°]	5.45–62.162	4.706–54.994	6.186–61.888
Total no. of reflns	8758	10339	5355
No. of indep reflns	3068	10339	3013
R	0.0657	0.0671	0.0540
wR_2	0.1114	0.2136	0.1362
S	1.057	1.183	1.118

factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC 1909553 (**3**), 190554 (**5**) and 190555 (**7**).

2.4. Reaction products

2.4.1. Synthesis of [$PdCl_2${PhC≡$CCH_2NC_4H_8NCH_2C$≡CPh}-κ^2-N,N] (**3**)

An ethanol solution (10 mL) of *1,4*-bis(3-phenylprop-2-yn-1-yl) piperazine (**1**) (0.050 g, 0.159 mmol) was added dropwise to a solution of $PdCl_2$ (0.028 g, 0.159 mmol) in the same solvent (10 mL) at room temperature. The resultant turbid solution was stirred further for 48 h. The solvent was removed under reduced pressure, to afford **3** as brown solid. The crystals suitable for SCXRD of **3** were obtained by slow diffusion of dichloromethane into the saturated solution of ethanol at room temperature. Yield: 76% (0.059 g). Mp: 232–235 °C. Anal. Calcd. for $C_{22}H_{22}Cl_2N_2Pd$: C, 53.74; H, 4.51; N, 5.70. Found: C, 53.76; H, 4.44; N, 5.75. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.4–7.28 (m, 10H, Ar–H), 3.57 (s, 4H, CH_2–N), 2.79 (s, 8H, CH_2–CH_2). ^{13}C{^{1}H} NMR (125.75 MHz, DMSO-d_6): δ 131.93 (Ar), 128.41(Ar), 128.35(Ar), 123.14(Ar), 85.91(C≡C), 84.11(C≡C), 51.99(CH_2), 47.80 (CH_2). FT-IR (KBr disk, cm^{-1}): 3454 (br), 3096 (w), 2925 (m), 2853 (w), 1662 (s), 1491 (m), 1445 (m), 1316 (w), 1261 (m), 1175 (w), 1073 (w), 1025 (m), 1001 (m), 762 (m), 700 (s).

2.4.2. Synthesis of [$PdCl_2${Me_3SiC≡$CCH_2NC_4H_8NCH_2C$≡$CSiMe_3$}-κ^2-N,N] (**4**)

An ethanol solution (15 mL) of *1,4*-bis(3-(trimethylsilyl)prop-2-yn-1-yl)piperazine (0.050 g, 0.163 mmol) was added dropwise to a solution of $PdCl_2$ (0.028 g, 0.163 mmol) in the same solvent (5 mL) at room temperature. The resultant turbid solution was stirred further for 48 h. The solvent was removed under reduced pressure, to afford **4** as brown solid. Yield: 76% (0.059 g). Mp: 221–223 °C. Anal. Calcd. for $C_{16}H_{30}Cl_2N_2PdSi_2 \cdot H_2O$: C, 38.28; H, 6.43; N, 5.58. Found: C, 38.52; H, 6.10; N, 5.65. FT-IR (KBr disk, cm^{-1}): 3446 (br), 2961 (s), 2481 (s), 1626 (s), 1428 (m), 1262 (m), 1073 (w), 1025 (m), 854 (m).

2.4.3. Synthesis of [$Pd_4(\mu$-Cl)$_4$(PhC=$C(Cl)CH_2NC_4H_8NCH_2$(Cl) C=CPh)$_2$] (**5**)

A mixture of $PdCl_2$ (0.056 g, 0.315 mmol) in ethanol (10 mL) was added dropwise to a solution of *1,4*-bis(3-phenylprop-2-yn-1-yl) piperazine (0.049 g, 0.157 mmol) also in the same solvent (5 mL) at room temperature. The resultant reaction mixture was stirred for further 48 h, concentrated to 2 mL and layered with dichloromethane (3 mL). The saturated yellowish-brown solution was stored at room temperature for 48 h to obtain **5** as yellowish-brown crystalline material. Crystals suitable for SCXRD of **5** were obtained by slow diffusion of dichloromethane into the saturated solution of ethanol at room temperature. Yield: 82% (0.087 g). Mp: 242–244 °C. Anal. Calcd. for $C_{44}H_{44}Cl_8N_4Pd_4 \cdot CH_2Cl_2$: C, 37.96; H, 3.26; N, 3.94. Found: C, 38.01; H, 3.28; N, 4.09 ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.30 (m, 20H, Ph–H), 4.18 (s, CH_2–N, 8H), 3.90 (d, $^3J_{HH}$ = 6.8 Hz, pip-CH_2, 8H), 3.04 (d, $^3J_{HH}$ = 6.8 Hz, pip-CH_2, 8H). ^{13}C {^{1}H} NMR (125.75 MHz, $CDCl_3$): δ 132.0 (Ph), 129.4 (Ph), 128.6 (Ph), 121.5 (Ph), 90.1(C=C–Cl), 78.7 (C=C), 55.1(pip-CH_2), 50.7 (CH_2–N). FT-IR (KBr disk, cm^{-1}): 3476 (br), 3056 (w), 2979 (m), 2930 (w), 2882 (m), 2445 (m), 2215 (m), 1618 (s), 1598 (s), 1491 (s), 1462 (m), 1442 (m), 1424 (m), 1390 (w), 1361 (m), 1342 (s), 1280 (m), 1204 (m), 1171 (m), 1073 (w), 1081 (s), 1029 (m) 920 (w), 799 (m), 758 (s), 691 (s), 666 (s).

2.4.4. Synthesis of [$Pd_4(\mu$-Cl)$_4$(Me_3SiC=$C(Cl)CH_2NC_4H_8NCH_2$(Cl) C=$CSiMe_3$)$_2$] (**6**)

This was synthesized by a procedure similar to that of **5**, using $PdCl_2$ (0.058 g, 0.326 mmol) and *1,4*-bis(3-(trimethylsilyl)prop-2-yn-1-yl)piperazine (0.050 g, 0.163 mmol). A 1:1 solution of (dichloromethane and petroleum ether) of **6** stored at room temperature for 24 h afforded analytically pure product of **6** as brown solid. Yield: 70% (0.073 g). Mp: 236–237 °C. Anal. Calcd. for $C_{32}H_{60}Cl_8N_4Pd_4Si_4 \cdot CH_2Cl_2$: C, 28.15; H, 4.44; N, 3.98. Found: C, 28.13; H, 4.54; N, 4.07. FT-IR (KBr disk, cm^{-1}): 3677 (w), 3467 (br), 2961 (s), 2181 (m), 1616 (s), 1454 (s), 1428 (s), 1363 (w), 1342 (w), 1250 (s), 1172 (m), 1090 (s), 1024 (s), 855 (s), 798 (m), 761 (m), 701 (w), 636 (m).

2.4.5. Synthesis of [{Cu(μ-I)}$_2$(PhC≡$CCH_2NC_4H_8NCH_2C$≡CPh)]$_n$ (**7**)

An acetonitrile solution (10 mL) of *1,4*-bis(3-phenylprop-2-yn-1-yl)piperazine (0.050 g, 0.159 mmol) was added dropwise to a solution of CuI (0.061 g, 0.318 mmol) in the same solvent (10 mL) at room temperature. The resultant turbid solution was stirred further for 48 h. The solvent was removed under reduced pressure, to obtain **7** as yellow solid. The crystals suitable for SCXRD of **7** were obtained by slow diffusion of acetonitrile into the saturated solution of dichloromethane at room temperature. Yield: 67% (0.074 g). Mp: 260–264 °C (dec). Anal. Calcd. for $C_{22}H_{22}Cu_2I_2N_2$: C, 38.00; H, 3.19; N, 4.03. Found: C, 38.35; H, 3.55; N, 3.78. FT-IR (KBr disk, cm^{-1}): 3449 (br), 3072 (m), 2913 (w), 2878 (m), 2841 (s), 2777 (w), 2240 (w), 1595 (m), 1488 (m), 1452 (m), 1441 (m), 1394 (w), 1366 (w), 1338 (s), 1304 (m), 1114 (s), 1103 (s), 1069 (w), 992 (w), 969 (w), 928 (w), 821 (s), 756 (s), 691 (s), 525 (w).

2.4.6. Synthesis of [{Cu(μ-I)}$_2$(Me_3SiC≡$CCH_2NC_4H_8NCH_2C$≡$CSiMe_3$)]$_n$ (**8**)

This was synthesized similar to that of **7**, by using CuI (0.062 g, 0.326 mmol) and *1,4*-bis(3-(trimethylsilyl)prop-2-yn-1-yl)piperazine (0.050 g, 0.163 mmol). Yield: 74% (0.083 g). Mp: 260–263 °C (dec). Anal. Calcd. for $C_{16}H_{30}Cu_2I_2N_2Si_2$: C, 27.95; H, 4.40; N, 4.07. Found: C, 28.32; H, 4.73; N, 4.19. FT-IR (KBr disk, cm^{-1}): 3736 (br), 2954 (s), 2837 (m), 2356 (w), 2168 (s), 1457 (m), 1327 (w), 1555 (s), 1054 (s), 984 (s), 969 (w), 845 (s), 758 (s).

2.4.7. Synthesis of [$Cu_2(\mu$-Cl)$_2$(PhC≡$CCH_2NC_4H_8NCH_2C$≡CPh)$_2$] (**9**)

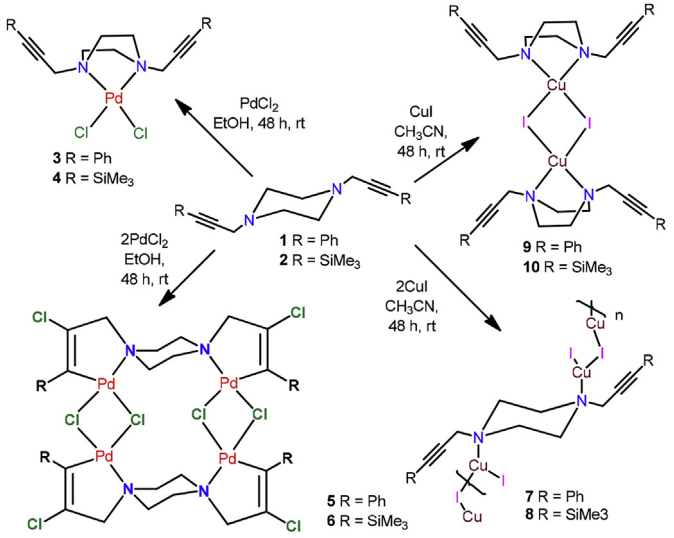
A mixture of CuI (0.032 g, 0.159 mmol) and *1,4*-bis(3-phenylprop-2-yn-1-yl)piperazine (0.050 g, 0.159 mmol) in acetonitrile (20 mL) was stirred at room temperature for 48 h. Then the solvent was removed under reduced pressure to afford yellow solid. The compound **9** was washed with diethyl ether (20 mL) and dried under vacuum to obtain analytically pure yellow solid. Yield: 84% (0.067 g). Mp: 247–249 °C (dec). Anal. Calcd. for $C_{44}H_{44}Cu_2I_2N_4$: C, 52.34; H, 4.39; N, 5.55. Found: C, 51.81; H, 4.46; N, 5.38. FT-IR (KBr disk, cm^{-1}): 3365 (br), 3248 (m), 2958 (m) 2922 (m), 2903 (m), 2837 (m), 2128 (m), 1658 (m), 1457 (m), 1428 (m), 1327 (m), 1315 (m), 1285 (w), 1254 (m), 1145 (m), 1122 (m), 1055 (w), 1006 (m), 985 (s), 842 (s), 794 (w), 758 (m), 730 (w), 699 (w), 637 (m), 568 (w).

2.4.8. Synthesis of [$Cu_2(\mu$-Cl)$_2$(Me_3SiC≡$CCH_2NC_4H_8NCH_2C$≡$CSiMe_3$)$_2$] (**10**)

This was synthesized by a procedure similar to that of **9**, by using CuI (0.031 g, 0.163 mmol) and 1,4-bis(3-(trimethylsilyl)prop-2-yn-1-yl)piperazine (0.050 g, 0.163 mmol). Yield: 81% (0.078 g). Mp: 253–255 °C (dec). Anal. Calcd. for $C_{32}H_{60}Cu_2I_2N_4Si_4$: C, 38.66; H, 6.08; N, 5.63. Found: C, 38.65; H, 6.34; N, 5.40. FT-IR (KBr disk, cm^{-1}): 3434 (br), 3056 (m), 2878 (s) 2845 (s), 2231 (m), 1742 (w), 1596 (w), 1489 (m), 1450 (s), 1329 (s), 1146 (s), 1115 (s), 994 (m), 816 (m), 750 (s), 683 (s), 521 (w), 464 (w).

3. Results and discussion

The reactions of **1** and **2** with one equivalent of $PdCl_2$ produced [$PdCl_2${PhC≡$CCH_2NC_4H_8NCH_2C$≡CPh}-κ^2-N,N] (**3**) and [$PdCl_2${Me_3



Scheme 1. The palladium(II) and copper(I) complexes of propargylamines.

$SiC{\equiv}CCH_2NC_4H_8N{-}\ CH_2C{\equiv}CSiMe_3\}$-$\kappa^2$-*N,N*] (**4**) in good yield. Similar reactions of **1** or **2** with two equivalents of $PdCl_2$ afforded chloropalladated products $[Pd_4(\mu\text{-}Cl)_4(PhC{=}C(Cl)CH_2NC_4H_8NCH_2(Cl)C{=}CPh)_2]$ (**5**) and $[Pd_4(\mu\text{-}Cl)_4(Me_3SiC{=}C(Cl)CH_2NC_4H_8NCH_2(Cl)C{=}CSiMe_3)_2]$ (**6**), respectively (Scheme 1). These complexes are sparingly soluble in most of the common organic solvents.

Treatment of **1** and **2** with two equivalents of CuI in acetonitrile afforded 2-D coordination polymers $[\{Cu_2(\mu\text{-}I)\}_2(PhC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CPh)]_n$ (**7**) and $[\{Cu(\mu\text{-}I)\}_2(Me_3SiC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CSiMe_3)]_n$ (**8**). Piperazine and $[Cu(\mu\text{-}I)]_2$ rhomboids are arranged in an alternate fashion *via* N–Cu linkage to form two dimensional polymeric sheets. Similarly, the reactions of **1** and **2** with one equivalent of CuI in acetonitrile afforded dicopper complexes $[Cu_2(\mu\text{-}I)_2(PhC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CPh)_2]$ (**9**) and $[Cu_2(\mu\text{-}I)_2(Me_3SiC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CSiMe_3)_2]$ (**10**), respectively (Scheme 1). These copper complexes are insoluble in most of the organic solvents. The perspective views of the molecular structures of **3**, **5** and **7** along with the atom numbering schemes are shown in Figs. 1–4, respectively.

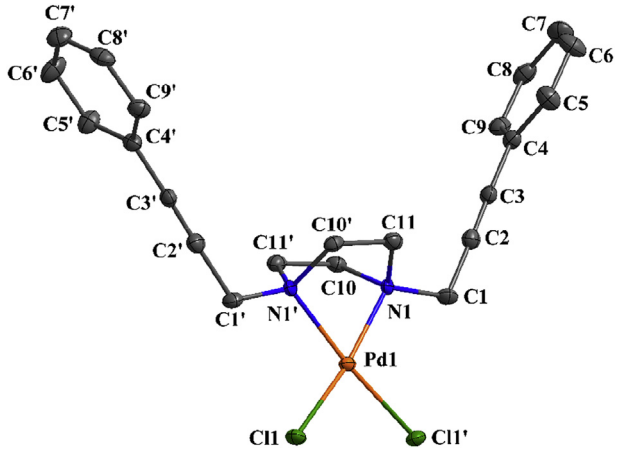


Fig. 1. Molecular structure of $[PdCl_2\{PhC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CPh\}$-$\kappa^2$-*N,N*] **3**. All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and bond angles (°): Pd1–N1 = 2.072(4), Pd1–Cl1 = 2.2933(13), N1–C1 = 1.480(6), N1–C10 = 1.493(5), N1–C11 = 1.510(6), C2–C1 = 1.485(7), C3–C2 = 1.181(7); N1–Pd1–N1' = 72.9(2), N1–Pd1–Cl1' = 98.16(12), N1–Pd1–Cl1 = 170.15(11), Cl1–Pd1–Cl1' = 91.01(7), C1–N1–C10 = 113.2(4), C10–N1–C11 = 107.(4)4, C3–C2–C1 = 177.5(6).

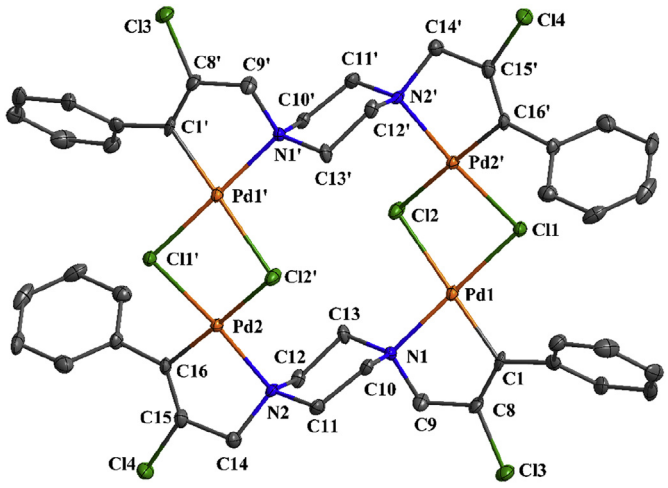


Fig. 2. Molecular structure of $[Pd_4(\mu\text{-}Cl)_4(PhC{=}C(Cl)CH_2NC_4H_8NCH_2(Cl)C{=}CPh)_2]$ (**5**). All hydrogen atoms and solvent molecules have been omitted for clarity. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and bond angles (°): Pd2–C16 = 2.002(7), Pd2–N2 = 2.101(6), Pd2–Cl1' = 2.3197(17), Pd2–Cl2' = 2.4345(18), Pd1–C1 = 1.989(6), Pd1–N1 = 2.089(6), Pd1–Cl1 = 2.3142(17), Pd1–Cl2 = 2.4186(18), Cl4–C15 = 1.752(7), Cl3–C8 = 1.750(7); C16–Pd2–N2 = 81.7(3), C16–Pd2–Cl1' = 93.9(2), N2–Pd2–Cl1' = 175.13(16),N2–Pd2–Cl2' = 100.73(16), Cl1'–Pd2–Cl2' = 83.50(6), C1–Pd1–N1 = 82.4(3), C1–Pd1–Cl1 = 96.2(2), N1–Pd1–Cl1 = 174.37(16), C1–Pd1–Cl2 = 176.6(2), N1–Pd1–Cl2 = 97.74(16), Pd1–Cl1–Pd2' = 92.54(6).

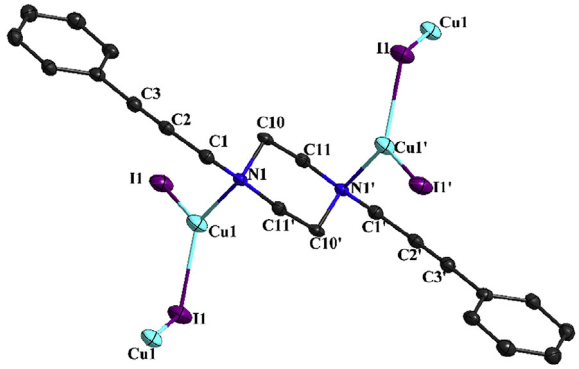


Fig. 3. Molecular structure of $[\{Cu(\mu\text{-}I)\}_2(PhC{\equiv}CCH_2NC_4H_8NCH_2C{\equiv}CPh)]_n$ **7**. All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level. Some selected bond distances (Å) and bond angles (°): I1–Cu1 = 2.5062(5), I1–Cu1' = 2.5381(5), Cu1–N1 = 2.053(3), N1–C1 = 1.497(5), N1–C10 = 1.496(4), N1–C11 = 1.482(5), C3–C2 = 1.196(6), C1–C2 1.461(6); Cu1–I1–Cu1' = 114.290(13), I1–Cu1–I1 = 116.289(18), N1–Cu1–I1 = 126.15(9), N1–Cu1–I1' = 117.47(9), C1–N1–Cu1 = 107.5(2), C1–N1–C10 = 109.2(3), C1–N1–C11 = 108.2(3), C10–N1–Cu1 = 111.6(2).

The crystallographic data and the details of structure determinations are given in experimental section and selected bond distances [Å] and bond angles [°] are listed in figure captions.

Slow diffusion of dichloromethane into an ethanolic solution of **3** led to the formation of yellowish-brown crystals suitable for single crystal X-ray diffraction study. The propargylamine coordinates through both the nitrogen atoms in *cis*-configuration by adopting boat conformation with Pd1–N1 and Pd1–Cl1 bond distances of 2.072(4) and 2.2933(13) Å, respectively. The bond angles N1–Pd1–N1' (72.9(2)°), N1–Pd1–Cl1' (98.16(12)°) and N1–Pd1–Cl1 (170.15(12)°) indicate the distorted square planar geometry around palladium atom. Both the acetylenes are in *cis*-configuration with respect to the piperazine ring. The C3–C2–C1 bond angle is 177.5(6)°.

Crystals suitable for SCXRD of $[Pd_4(\mu\text{-}Cl)_4(PhC{=}C(Cl)CH_2NC_4H_8NCH_2(Cl)C{=}CPh)_2]$ (**5**) were obtained by slow diffusion of

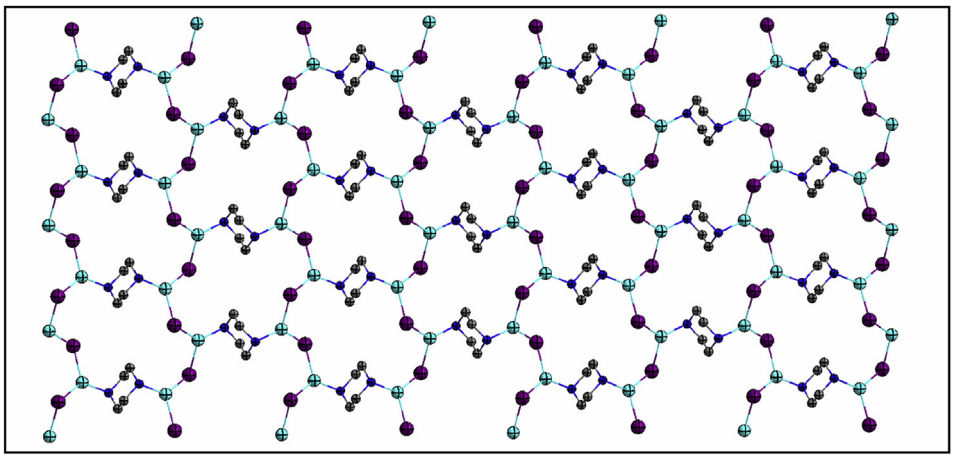


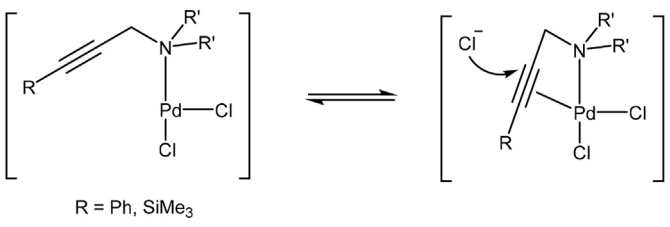
Fig. 4. The core of 2-D polymeric structure of **7**. All the hydrogen atoms and phenylacetylene fragments are omitted for clarity.

dichloromethane into the saturated solution in ethanol at room temperature. The piperazine rings adopt chair conformations in which both the nitrogen atoms coordinate to two different palladium centers while in complex **3** piperazine adopted the boat conformation. The *trans*-chloropalladation occurs due to the activation of acetylene triple bond and nitrogen coordination to palladium atom forming a tetrapalladium complex [20]. The coordination sphere of Pd1 including the C3, N1, Cl1 and Cl2 atoms can be considered as essentially planar. The angles of C1—Pd1—Cl1 (96.2(2)°), N1—Pd1—Cl2 (97.74(16)°), and C1—Pd1—N1 (82.4(3) °) indicate distorted square planar geometry around palladium. The Pd—C, Pd—N, Pd—Cl bond distances and N—Pd—C, and Cl—Pd—Cl bond angles in **5** are similar to the analogous dinuclear chloropallladated complexes reported in the literature [16,21]. Both the palladium atoms are coordinated with bridging chloride ions to forms a four membered ring with Pd1—Cl1—Pd2' angle of 92.54(6)°. The *trans*-stereochemistry at the C1—C8 vinyl bond between Cl3 and the palladium centre is noteworthy with Cl3—C8 bond distance of 1.750(7) Å. Two types of mechanisms have been proposed to explain the stereo-chemical outcome in the chloropalladation reaction of various substituted alkynes. The first one involves the intramolecular insertion of the acetylene triple bond into the Pd—Cl bond to give the kinetic product *via cis*-chloropalladation. However, in some cases, it leads to the thermodynamically more stable *trans*-chloropalladated isomers. In the second mechanism, the reaction proceeds *via* an external nucleophilic attack of the chloride ion onto the activated triple bond, affording the *trans*-isomer.

The mechanism can be operative, depending upon the nature of alkyne substituents and the reaction conditions [26,49–52]. The second mechanism, involving an intermolecular nucleophilic attack of the chloride ion onto the palladium activated C≡C bond (Scheme 2), stems from the results observed in the case of propargylamines. The formation of five-membered palladacycle is through the activation of electrophilic carbon-carbon triple bond. The stability of palladacycle conformation depends on the nature of the hetero atom substituents.

Slow diffusion of acetonitrile into a dichloromethane solution of **7** led to the formation of crystals suitable for X-ray analysis. The core structure of **7** consists of 2-D polymeric sheet in which the piperazine nitrogen atoms are coordinated to [Cu(μ-I)Cu] rhombic unit and propagate in a linear fashion. The copper centers in **7** are tri-coordinated and adopt distorted trigonal geometry around copper atoms. The piperazine ring adopts *trans*-conformation and both the acetylene moieties are also *trans* with respect to piperazine ring. The I1—Cu1 (2.5062(5) Å) and I1—Cu1' (2.5381(5) Å) bond distances show very little difference for non-bridging and bridging iodides. The Cu—N bond distance is Cu1—N1 2.053(3)Å. The N1—Cu1—I1 bond angle around copper centre is 126.15(9)°. The bond parameters of **7** matches with those in analogous copper polymers [Cu(κ^2-*P,P'*-DPEphos)(μ-4,4′-bpy)]*n*[BF_4]$_n$ [53,54].

Powder X-ray diffraction (PXRD) pattern was recorded with Cu Kα radiation ($\lambda = 1.54184$ Å) source at room temperature. The purity of the bulk powdered sample is ascertained by the PXRD diffraction peaks relevant to those are calculated from single crystal X-ray data (Fig. 5). However, the intensities of the diffraction peaks of complex **7** marginally differ from its calculated spectrum [55]. As depicted in Fig. 5, the PXRD patterns of complex **7** reveals broader patterns, which might be due to one or more stacking faults [56] occurred due to grinding effect, during the sample preparation for the PXRD analysis. As a result, change in both the peak profile and the peak position [41,44,57–59] was observed. In addition, the appearance of broader peaks may likewise be due to the amorphous nature of the bulk sample.



Scheme 2. Possible mechanism for chloropalladation reaction.

4. Conclusions

In summary, the synthesis of functionalized propargylamines and their coordination complexes with Cu^{I} and Pd^{II} are described. The ligand to metal ratio plays an important role in these reactions. The ligands to palladium ratio of 1:1 afforded simple κ^2-*N,N*-coordinated chelate complexes, whereas 1:2 reactions resulted in chloropalladated tetranuclear complexes in good yields. Similar reactions with square-planar CuI also yielded κ^2-*N,N*-coordinated Cu^{I} dimers having [Cu(μ_2-I)]$_2$ rhombus units as well as 2-D coordination polymers. In the case of 2-D coordination polymer, the propagation of polymeric chain involves [Cu(μ_2-I)Cu] units in a linear fashion. Since the utility of cyclopalladated intermediates in

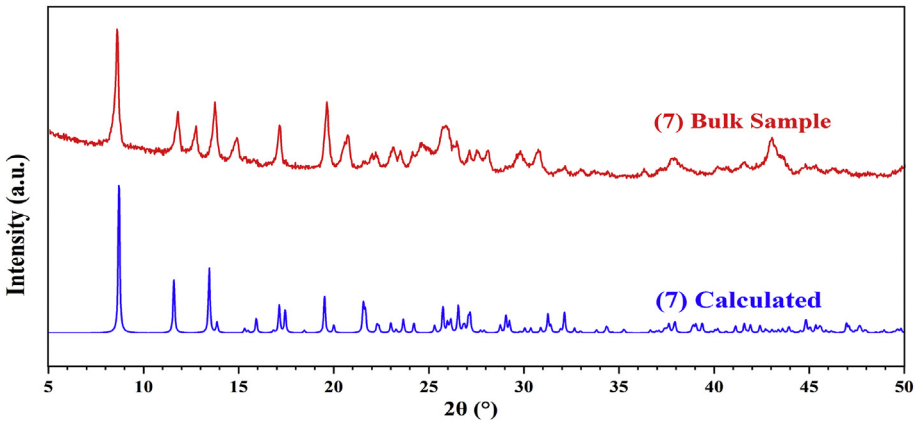


Fig. 5. PXRD (Cu Kα) of **7** measured at room temperature bulk sample and calculated from the single crystal data recorded at 150 K.

various organic transformations are well documented, the isolated and structural characterization of tetranuclear complexes provide useful information about the reaction pathways and mechanisms. The functionalized propargylamines having acetylene groups as pendant side arms can act as $2e^-$ or $4e^-$ donors, upon treatment with suitable metal precursors, further work in this direction and also exploration of palladium complexes in hydrochlorination of alkenes are underway.

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Supporting Information

NMR and IR spectra, crystallographic data, and CIFs for the structure determination of **3**, **5** and **7** are given. This material is available free of charge via the www.elsevier.com/locate/jorganchem. CCDC 1909553 (**3**), 190554 (**5**) and 190555 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.07.006.

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