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Novel Trisphosphine Ligand Containing 1,3,5-Triazine Core, [2,4,6-$C_3N_3\{C_6H_4PPh_2\text{-}p\}_3$]: Synthesis and Transition Metal Chemistry

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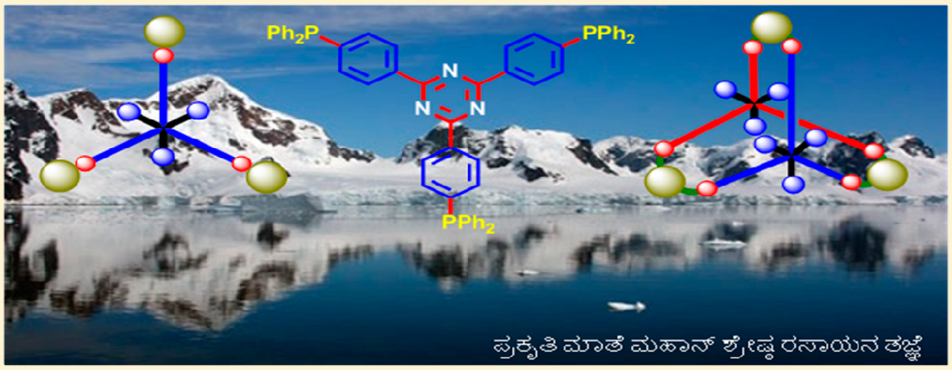
Supporting Information



ABSTRACT: The trisphosphine ligand with triazine core, 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine (**2**), was synthesized in moderate yield by reacting 2,4,6-tris(4-bromophenyl)-1,3,5-triazine with 3 equiv of $KPPh_2$. The tris(phosphine) **2** undergoes facile oxidation to give trischalcogenides 2,4,6-$C_3N_3\{C_6H_4P(E)Ph_2\text{-}p\}_3$ (E = O, **3**; S, **4**; Se, **5**) on treatment with aqueous H_2O_2, elemental sulfur, or selenium. The reaction between **2** and [$AuCl(SMe_2)$] yielded a trinuclear complex, [$(AuCl)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$] (**6**), which on further treatment with pyridyl ligands such as 2,2′-bipyridine (2,2′-bpy) and 1,10-phenanthroline (1,10-phen) produced the mixed-ligand complexes [$\{Au(2,2'\text{-bpy})\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$]-$(OTf)_3$ (**7**) and [$\{Au(1,10\text{-phen})\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$]$(OTf)_3$ (**8**), where OTf indicates trifluoromethansulfonate. Several trimetallic complexes such as [$\{Ru(\eta^6\text{-cymene})Cl_2\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$] (**9**), [$\{Pd(\eta^3\text{-}C_3H_5)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$] (**10**), [$\{Rh(COD)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$] (**11**) and [$\{Ir(COD)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}$] (**12**) have also been synthesized and characterized. The reactions of **2** with [$M(COD)Cl_2$] and CuI afforded metallocyclophane type complexes, [$(MCl_2)_3L_2$] (M = Pd; **13**, Pt; **14**) (L = 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine) and [$(CuI)_3L_2$] (**15**), in good yield.

INTRODUCTION

The burgeoning interest in the synthesis and coordination chemistry of compounds containing the 1,3,5-triazine core is mainly due to the core's planar geometry with 3-fold symmetry, which is ideally suited for generating highly symmetrical metal−organic frameworks with diverse structures[1−4] and wide applications.[5−11] In the field of supramolecular and material chemistry, the trispyridine derivative, 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) (**I**), has been extensively used to make complexes all the way from simple trinuclear molecules[12−17] to zeolite-type structures as well as molecular prisms,[18−23] cyclophane-type host−guest complexes,[24−26] metal-directed, self-assembled molecular cages,[27−29] tubes, and box-type[30] structures. Triazine derivatives also support hydrogen bonds and favor $\pi-\pi$ contacts as well.[31−34] The presence of additional noncovalent forces in triazine-based aggregates makes it possible to generate tubular fibres[35] or three-dimensional (3D) porous networks.[36−39] Apart from the thoroughly explored tpt, other triazine derivatives employed in supramolecular chemistry are triscarboxylates,[40,41] trisacetylene,[42] trisamines,[43−48] tris(polyborate),[49] and trisalkyl or aryl derivatives.[45,50] A few representative derivatives (**I**−**VIII**) are given in Chart 1.

Surprisingly, to date, there is no report on triazines appended with phosphorus(III) functionalities as these ligands can coordinate to even low-valent metals at the periphery, giving simple trimetallic complexes, cyclophane-type cages or one-dimensional (1D) and two-dimensional (2D) coordination polymers. Furthermore, there are not many trisphosphines with C_3-symmetry that can be used to make 3D coordination polymers with late transition metals, especially in their low valent states. Therefore, it would be interesting to explore such systems in material applications[51,52] and also in homogeneous[53] as well as heterogeneous catalysis. Although the similar trisphosphine, 1,3,5-$C_3N_3(PPh_2)_3$ (**VIII**),[54] and its silver complexes[55−58] have been reported, the corresponding phenyl

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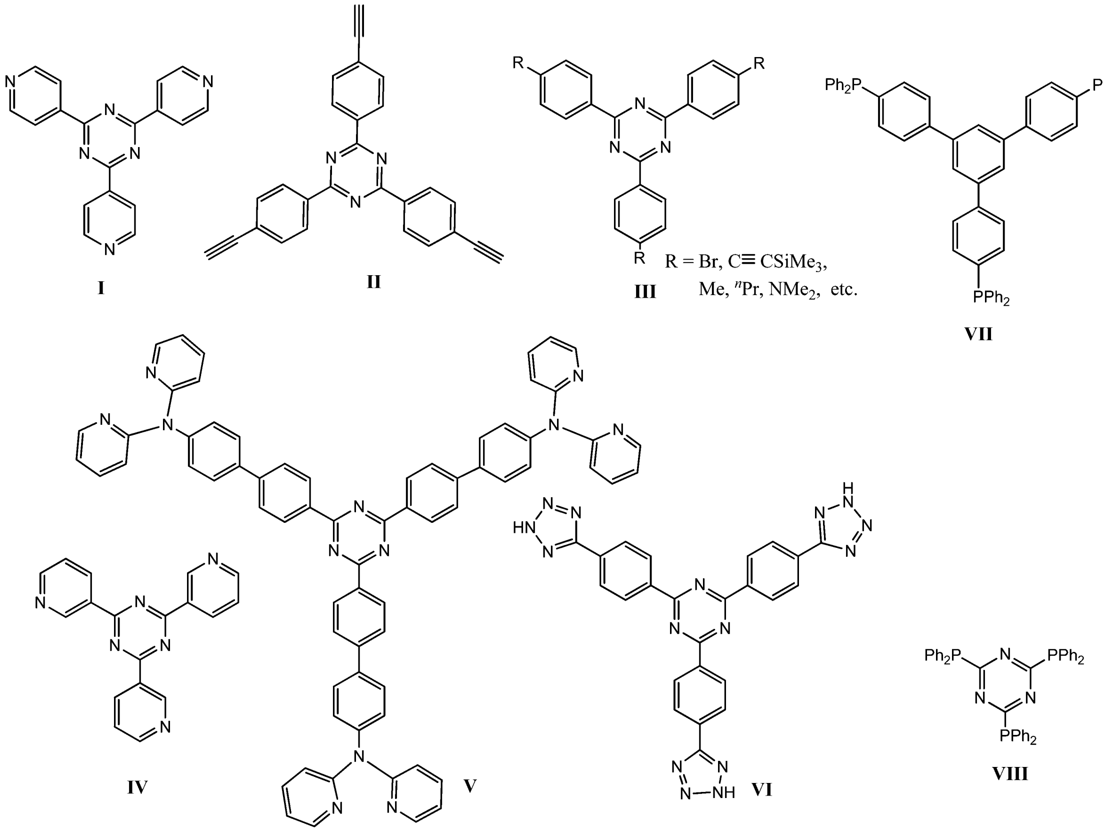
Chart 1. Various Triazine Derivatives



derivative, 1,3,5-C_6H_3-2,4,6-($C_6H_4PPh_2$-*p*)$_3$ (**VII**), has been reported very recently.[59] As an extension of our interest[60−64] and the interest of others[12,55,56] in highly symmetrical polyphosphanes, we have sought to prepare triazine-based trisphosphines to explore their coordination chemistry. In this Paper, we report the synthesis and transition-metal chemistry of trisphosphine, [2,4,6-C_3N_3{$C_6H_4PPh_2$-*p*}$_3$]. The crystal structures of two cyclophane-type derivatives with platinum(II) and copper(I) are also described.

■ EXPERIMENTAL SECTION

General Considerations. All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use. The compounds [AuCl(SMe$_2$)],[65] [Ru(η^6-cymene)Cl$_2$]$_2$,[66] [M(COD)Cl]$_2$ (M = Rh or Ir),[67] [M(COD)Cl$_2$] (M = Pd or Pt),[68] and [Pd(η^3-C_3H_5)Cl]$_2$[69] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. Solution NMR spectra were recorded on a Bruker AV-400 or AV-500 MHz spectrometer at ambient probe temperatures. Solid state ^{31}P NMR spectra were recorded on the Bruker AV-500 MHz spectrometer with magic angle spinning (MAS) at 15 kHz. NMR shifts are given in δ with positive values downfield of tetramethylsilane (^{1}H and ^{13}C), external H_3PO_4 (^{31}P), and external ammonium dihydrogen phosphate reference (solid state ^{31}P, δ 0). The ^{13}C and ^{31}P NMR spectra were recorded in proton-decoupled mode. Positive values indicate downfield shifts. Infrared (IR) spectra were recorded on a Nicolet Impact 400 Fourier trasform (FT) IR instrument in a KBr disk or a nujol mull. Microanalyses were carried out on a Carlo Erba (model 1106) elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker instrument with Cu Kα radiation in the 2θ range of 5−90° at 293 K. Melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected.

Synthesis of 2,4,6-C_3N_3($C_6H_4PPh_2$-*p*)$_3$ (2). (a) To a vigorously stirred solution of trifluoromethane sulfonic acid (2 mL, 22.7 mmol) in dry chloroform (5 mL) cooled to 0 °C under a stream of nitrogen was added dropwise a solution of 4-bromobenzonitrile (2 g, 11 mmol) in dry chloroform. The reaction mixture was slightly exothermic upon addition of the latter solution. The yellow-colored reaction mixture was stirred at 0 °C for 2 h, and stirring was continued for 24 h at ambient temperature. The solution was poured into water containing a small amount of ammonium hydroxide. The organic layer was washed four times with water and then dried over sodium sulfate. The solvent was evaporated under vacuum, and the residue was recrystallized from chloroform.

(b) To freshly cut potassium (1.45 g, 37.2 mmol) in tetrahydrofuran (THF) (40 mL) at −78 °C was added diphenylphosphine (2.18 g, 12 mmol) also in THF (15 mL). The resulting reddish orange-colored solution was stirred at the same temperature for 8 h. It was filtered, and the filtrate was added dropwise through a cannula to a suspension of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (2 g, 3.7 mmol) in 60 mL of THF at −78 °C. After the completion of the addition, the reaction mixture was warmed to room temperature. Stirring was continued for 12 h, and then the solution was refluxed for 48 h. The reaction mixture was filtered through a frit with a 4 cm Celite bed. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane and passed through a silica column. The solvent was removed under reduced pressure, and the residue was crystallized from dichloromethane to obtain a white crystalline product. Yield: 40% (1.26 g). Mp: 260−262 °C. IR (KBr): 3069 (w), 2962 (w), 1919 (w), 1591 (sh), 1579 (s), 1512(s), 1400(s), 1366(s), 1260(s), 1171 (s), 1100 (w), 1068 (s), 1010 (w), 802 (s), 694 (w) cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$), δ: −5.1 (s). ^{1}H NMR (CDCl$_3$), δ: 8.65 (d, CH, 6H, $^3J_{HH}$ = 7.6 Hz), 7.37−7.46 (m, ArH, 36H). ^{13}C NMR (CDCl3, 125.7 MHz), δ: 171.318 (s), 138.812 (s), 132.502 (d, J_{PC} = 10.06 Hz), 132.385 (s), 132.226 (s), 132.058 (d, J_{PC} = 9.9 Hz), 131.552 (s), 128.819 (d, J_{PC} = 12 Hz), 128.648 (d, J_{PC} = 12

Hz). Anal. Calcd for $C_{57}H_{42}N_3P_3$: C, 79.43; H, 4.91; N, 4.87. Found: C, 79.67; H, 4.87; N, 5.02%.

Synthesis of 2,4,6-C_3N_3\{$C_6H_4P(O)Ph_2$-*p*\}$_3$ (3). A 30% solution of hydrogen peroxide (0.0038 g, 0.105 mmol) in THF (5 mL) was added dropwise to a solution of **2** (0.03 g, 0.035 mmol) also in THF (5 mL) at room temperature, and the reaction mixture was stirred for 6 h. The solvent was evaporated, and the residue obtained was washed with petroleum ether and dried under vacuum to yield an analytically pure product of **3** as a white solid. Yield: 83% (0.026 g). Mp: >270 °C. IR (KBr): 2230 (w), 1672 (w), 1573 (w), 1516 (s), 1371 (w), 1180 (m), 1118 (m), 909 (s), 812 (w), 733 (s), 646 (w), 558 (m), 546 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 28.9 (s). ^1H NMR ($CDCl_3$), δ: 8.81 (d, CH, 6H, $^3J_{HH}$ = 8.4 Hz), 7.48−7.92 (m, ArH, 36H). Anal. Calcd for $C_{57}H_{42}N_3P_3O_3$: C, 75.24; H, 4.65; N, 4.62. Found: C, 75.47; H, 4.61; N, 4.72%.

Synthesis of 2,4,6-C_3N_3\{$C_6H_4P(S)Ph_2$-*p*\}$_3$ (4). A mixture of **2** (0.03 g, 0.035 mmol) and 3 equiv of elemental sulfur (0.0036 g, 0.112 mmol) in toluene (15 mL) was refluxed for 16 h. The colorless solution was filtered through a frit containing Celite. The filtrate was reduced to 7 mL and kept at −10 °C to get colorless X-ray quality crystals of **4**. Yield: 78% (0.026 g). Mp: 220−240 °C. IR (KBr): 2963 (m), 2816 (w), 1599 (s), 1515 (s), 1435 (s), 1353 (s), 1261 (s), 1099 (s), 1017 (s), 880 (w), 806 (s), 705 (s), 645 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 43.1 (s). ^1H NMR ($CDCl_3$) δ: 8.76 (d, CH, 6H, $^3J_{HH}$ = 7.6 Hz), 7.47−7.94 (m, ArH, 36H). ^{13}C NMR (CDCl3, 125.7 MHz), δ: 171.50 (s), 138.69 (s), 132.95 (d, J_{PC} = 10.06 Hz), 132.82 (s), 132.48 (d, J_{PC} = 10.06 Hz), 132.31 (s), 132.0 (s), 129.05 (d, J_{PC} = 12.57 Hz), 128.86 (d, J_{PC} = 12.57 Hz). Anal. Calcd for $C_{57}H_{42}N_3P_3S_3$: C, 71.46; H, 4.42; N, 4.39; S, 10.04. Found: C, 71.64; H, 4.39; N, 4.34; S, 9.82%.

Synthesis of 2,4,6-C_3N_3\{$C_6H_4P(Se)Ph_2$-*p*\}$_3$ (5). This was prepared in an analogous manner to **4**, using a mixture of **2** (0.03 g, 0.035 mmol) and 3 equiv of elemental selenium (0.009 g, 0.112 mmol) in toluene (15 mL). Yield: 76% (0.0292 g). Mp: >270 °C. IR (KBr): 3060 (w), 2963 (w), 1919 (w), 1579 (sh), 1515 (s), 1398 (w), 1368 (m), 1261 (m), 1096 (s), 805 (s), 706 (m), 693 (m), 567 (m), 526 (w) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 35.1 (s, $^1J_{PSe}$ = 736 Hz). ^1H NMR ($CDCl_3$), δ: 8.70 (d, CH, 6H, $^3J_{HH}$ = 8.4 Hz), 7.31−7.91 (m, ArH, 36H). Anal. Calcd for $C_{57}H_{42}N_3P_3Se_3$: C, 62.31; H, 3.85; N, 3.82. Found: C, 62.67; H, 3.77; N, 3.78%.

Synthesis of [(AuCl)$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}] (6). A solution of [AuCl(SMe_2)] (0.0256 g, 0.087 mmol) in dichloromethane (5 mL) was added dropwise to the solution of **2** (0.025 g, 0.029 mmol) also in dichloromethane (5 mL), and the reaction mixture was stirred for 6 h. The clear solution thus obtained was concentrated to 3 mL; 1 mL of petroleum ether was added, and the mixture was stored at 0 °C for 24 h to yield the analytically pure product **6** as a colorless solid. Yield: 92% (0.0413 g). Mp: >275 °C. IR (KBr): 3059 (w), 2239 (w), 1573 (w), 1515 (s), 1437w (s), 1371 (m), 1102 (m), 910 (s), 811 (w), 733 (s), 695 (sh), 552 (m), 524 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 33.0 (s). ^1H NMR ($CDCl_3$), δ: 8.79 (d, CH, 6H, $^3J_{HH}$ = 8.4 Hz), 7.27−7.74 (m, ArH, 36H). ^{13}C NMR (CDCl3, 125.7 MHz), δ: 171.15 (s), 138.71 (s), 132.95 (d, J_{PC} = 10.06 Hz), 132.82 (s), 132.48 (d, J_{PC} = 10.06 Hz), 132.31 (s), 132.0 (s), 129.05 (d, J_{PC} = 12.57 Hz), 128.86 (d, J_{PC} = 12.57 Hz). Anal. Calcd for $C_{57}H_{42}N_3P_3Au_3Cl_3$: C, 43.91; H, 2.71; N, 2.69. Found: C, 43.60; H, 2.61; N, 2.76%.

Synthesis of [\{Au(2,2′-bipyridine)\}$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}](OTf)$_3$ (7). A solution of [AuCl(SMe_2)] (0.0256 g, 0.087 mmol) in dichloromethane (5 mL) was added dropwise to the solution of **2** (0.025 g, 0.029 mmol) in the same solvent (5 mL) and stirred for 2 h. Solid AgOTf (0.0224 g, 0.087 mmol) (OTF indicates trifluoromethanesulfonate) was added, and the stirring was continued for another 2 h. The AgCl precipitate formed was removed by filtration, and the filtrate was added to a solution of 2,2′-bipyridine (2,2′-bpy) (0.0136 g, 0.087 mmol) in dichloromethane (5 mL) and stirred overnight. The solvent was evaporated, washed with petroleum ether, and dried under reduced pressure to form the analytically pure product **7** as a white solid. Yield: 78% (0.0434 g). Mp: >280 °C. IR (KBr): 3057 (s), 2960 (w), 1591 (m), 1573 (m), 1514 (s), 1438 (s),1357 (m), 1263 (s), 1152 (m), 1100 (s), 1030 (m), 844 (w), 811 (m), 765 (m), 694 (m), 637 (m), 552 (m), 519 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 35.7 (s). ^1H NMR ($CDCl_3$), δ: 8.91 (d, bpy-3-H, 6H, $^3J_{HH}$ = 6.8 Hz), 8.53 (d, bpy-6-H, 6H, $^3J_{HH}$ = 7.6 Hz), 8.74 (d, ArH, 6H, $^3J_{HH}$ = 4.8 Hz), 8.22 (t, bpy-5-H, 6H, $^3J_{HH}$ = 7.6 Hz), 7.42−7.85 (m, ArH, bpy-4-H, 42H), 5.46 (solvated CH_2Cl_2). ^{13}C NMR (CDCl3), δ: 122.9−119.1 (m, OTf). Anal. Calcd for $C_{90}H_{66}N_9P_3S_3Au_3F_9O_9\cdot CH_2Cl_2$: C, 44.54; H, 2.79; N, 5.14; S, 3.92. Found: C, 44.84; H, 2.71; N, 5.01; S, 4.12%.

Synthesis of [\{Au(1,10-phenanthrolene)\}$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}](OTf)$_3$ (8). This was prepared in an analogous manner to compound **7**, using a solution of [AuCl(SMe_2)] (0.0256 g, 0.087 mmol), **2** (0.025 g, 0.29 mmol), AgOTf (0.014 g, 0.087 mmol), and 1,10-phenanthrolene (1,10-phen) (0.017 g, 0.087 mmol). Yield: 70% (0.063 g). Mp: >280 °C. IR (KBr): 3047 (s), 2961 (sh), 2335 (s), 1597 (m), 1572 (m), 1541 (sh), 1511 (s), 1461 (s), 1369 (m), 1259 (s), 1162 (s), 1100 (s), 1031 (s), 885 (w), 849 (s), 707 (sh), 694 (s), 638 (s), 550 (s), 552 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 35.8 (s). ^1H NMR ($CDCl_3$), δ: 9.11(br s, phen-2,9-H, 6H), 8.94 (d, CH, 6H, $^3J_{HH}$ = 7.2 Hz), 8.76 (br s, phen-4,7-H, 6H), 8.19 (s, phen-5,6-H,6H), 8.09 (br s, phen-3,8-H, 6H), 7.63−7.89 (m, ArH, 36H), 5.43 (solvated CH_2Cl_2). ^{13}C NMR (CDCl3), δ: 122.4 (m, OTf). Anal. Calcd for $C_{96}H_{66}N_9P_3S_3Au_3F_9O_9\cdot CH_2Cl_2$: C, 46.13; H, 2.71; N, 4.99; S, 3.81. Found: C, 46.35; H, 2.72; N, 4.76; S, 3.69%.

Synthesis of [\{Ru(η^6-cymene)Cl_2\}$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}] (9). A solution of [Ru(η^6-cymene)Cl_2]$_2$ (0.0263 g, 0.043 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **2** (0.0247 g, 0.0286 mmol) also in dichloromethane (5 mL). The resulting red reaction mixture was stirred overnight, the solution was concentrated to 3 mL, and petroleum ether was added to generate a reddish orange-colored precipitate. The solvent was evaporated, and the residue was washed with petroleum ether and dried under reduced pressure to form the analytically pure product **9** as a red solid. Yield: 81% (0.0423 g). Mp: >280 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 24.7 (s). ^1H NMR ($CDCl_3$), δ: 8.64 (d, CH, 6H, $^3J_{HH}$ = 6.8 Hz), 7.39−8.04 (m, ArH, 36H), 5.42 (solvated CH_2Cl_2), 5.23 (d, cym ArH, 6H, $^3J_{HH}$ = 6.4 Hz), 5.03 (d, cym ArH, 6H, $^3J_{HH}$ = 5.6 Hz), 2.87 (sept, CH, 3H), 1.91 (s, CH_3, 9H), 1.11 (d, CH_3, 18H, $^3J_{HH}$ = 6.8 Hz). Anal. Calcd for $C_{90}H_{93}N_3P_3Ru_3Cl_6\cdot CH_2Cl_2$: C, 57.21; H, 5.01; N, 2.20. Found: C, 57.32; H, 5.16; N, 2.28%.

Synthesis of [\{Pd(η^3-C_3H_5)Cl\}$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}] (10). A solution of [Pd(η^3-C_3H_5)Cl]$_2$ (0.013 g, 0.035 mmol) in dichloromethane (5 mL) was added dropwise to the solution of **2** (0.02 g, 0.023 mmol) in dichloromethane (5 mL) with constant stirring. The resulting yellow reaction mixture was stirred overnight. The solvent was evaporated, and the residue was washed with petroleum ether and dried under reduced pressure to form the analytically pure product **10** as a yellow solid. Yield: 83% (0.0272 g). Mp: >270 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 22.8 (s). ^1H NMR ($CDCl_3$), δ: 8.75 (d, CH, 6H, $^3J_{HH}$ = 7.6 Hz), 7.45−7.88 (m, ArH, 36H), 5.67−5.77 (m, CH, 3H), 5.43 (d, CH_2, 6H, $^3J_{HH}$ = 2.8 Hz), 1.26 (d, CH_3, 9H, $^3J_{HH}$ = 4.8 Hz). ^{13}C NMR (CDCl3, 125.7 MHz), δ: 171.49 (s), 138.32 (s), 137.71 (d, J_{PC} = 1.6 Hz), 134.43 (s), 134.26 (d, J_{PC} = 15.8 Hz), 132.30 (d, J_{PC} = 9.7 Hz), 131.99 (s), 131.05 (s), 128.91 (d, J_{PC} = 16.9 Hz), 118.44 (d, J_{PC} = 5 Hz), 80.47 (d, J_{PC} = 4.7 Hz), 61.56 (s). Anal. Calcd for $C_{66}H_{60}N_3P_3Pd_3Cl_3$: C, 56.07; H, 4.27; N, 2.97. Found: C, 55.87; H, 4.15; N, 3.08%.

Synthesis of [\{Rh(COD)Cl\}$_3$\{2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$\}] (11). A solution of [Rh(COD)Cl]$_2$ (0.026 g, 0.053 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **2** (0.0306 g, 0.035 mmol) in the same solvent (5 mL) with constant stirring. The resulting yellow-colored reaction mixture was stirred overnight; the solution was concentrated to 3 mL, and a few drops of petroleum ether were added to yield the analytically pure product **11** as a yellow crystalline solid. Yield: 83% (0.0465 g). Mp: 179−180 °C. IR (KBr): 3054 (w), 2962 (w), 1978 (m), 1572 (w), 1514 (s), 1436 (w), 1358 (m), 1261 (s), 1174 (w), 1097 (m), 1017 (m), 808 (s), 714 (m), 695 (m), 558 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 30.9 (d, $^1J_{RhP}$ = 150.6 Hz). ^1H NMR ($CDCl_3$), δ: 8.69 (d, CH, 6H, $^3J_{HH}$ = 7.04 Hz), 7.42−7.88 (m, ArH, 36H), 3.19 (br s, CH, 12H), 1.95 and 2.09 (d, CH_2, 24H). Anal. Calcd for $C_{81}H_{78}N_3P_3Rh_3Cl_3$: C, 60.75; H, 4.91; N, 2.62. Found: C, 60.53; H, 5.02; N, 2.51%.

Synthesis of [{Ir(COD)Cl}$_3${2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$}] (12). This was prepared in an analogous fashion to compound **11**, using [Ir(COD)Cl]$_2$ (0.033 g, 0.049 mmol) and **2** (0.0282 g, 0.033 mmol). Yield: 81% (0.049 g). Mp: >275 °C. IR (KBr): 3056 (w), 2962 (m), 2022 (m), 1572 (w), 1514 (s), 1436 (w), 1399 (w), 1358 (w), 1261 (m), 1095 (s), 1026 (sh), 803 (s), 696 (m), 547 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 22.1 (s). ^1H NMR ($CDCl_3$), δ: 8.71 (d, CH, 6H, $^3J_{HH}$ = 8.2 Hz), 7.43−7.85 (m, ArH, 36H), 5.23 (br s, CH, 12H), 1.61 and 1.89 (d, CH_2, 24H). Anal. Calcd for $C_{81}H_{78}N_3P_3Ir_3Cl_3$: C, 52.04; H, 4.20; N, 2.25. Found: C, 52.27; H, 4.25; N, 2.37%.

Synthesis of [$(PdCl_2)_3${2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$}$_2$] (13). A mixture of **2** (0.03 g, 0.035 mmol) and [Pd(COD)Cl_2] (0.015 g, 0.052 mmol) in dichloromethane (15 mL) was stirred under reflux overnight. It was cooled to room temperature, and the solvent was removed under reduced pressure to give the analytically pure product **13** as a yellow solid. Yield: 73% (0.0285 g). Mp: >280 °C. IR (KBr): 3052 (w), 2924 (w), 1599 (m), 1572 (m), 1514 (vs), 1436 (m), 1369 (m), 1262 (w), 1186 (w), 1095 (m), 810 (w), 743 (w), 694 (s), 530 (w) cm^{-1}. Cross-polarization (CP)-MAS ^{31}P NMR δ: 24.79 (s). Anal. Calcd for $C_{114}H_{84}N_6P_6Pd_3Cl_6$: C, 60.70; H, 3.75; N, 3.73. Found: C, 60.87; H, 3.67; N, 3.68%.

Synthesis of [$(PtCl_2)_3${2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$}$_2$] (14). This was prepared in an analogous fashion to comopund **13**, using compound **2** (0.030 g, 0.035 mmol) and [Pt(COD)Cl_2] (0.0195 g, 0.052 mmol). Yield: 78% (0.034 g). Mp: >280 °C. IR (KBr): 3054 (m), 2959 (sh), 1630 (sh), 1600 (m), 1506 (s), 1436 (s), 1360 (s), 1261 (w), 1189 (w), 1094 (s), 1016 (m), 842 (w), 809 (m), 744 (m), 701 (s), 535 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (DMSO-d_6), δ: 13.5 (s, $^1J_{PtP}$ = 3734 Hz). CP-MAS ^{31}P NMR δ: 16.1 (s, $^1J_{PtP}$ = 3719 Hz). Anal. Calcd for $C_{114}H_{84}N_6P_6Pt_3Cl_6$: C, 54.30; H, 3.36; N, 3.33. Found: C, 54.29; H, 3.31; N, 3.21%.

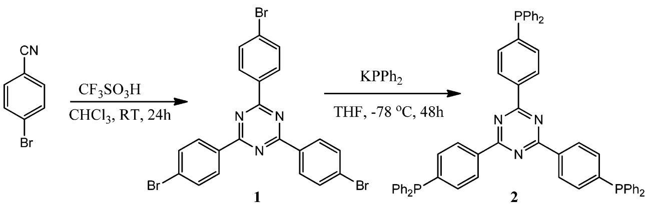
Synthesis of [$(CuI)_3${2,4,6-C_3N_3 ($C_6H_4PPh_2$-*p*)$_3$}$_2$] (15). A solution of CuI (0.0151 g, 0.052 mmol) in acetonitrile (5 mL) was added dropwise to a solution of ligand **2** (0.030 g, 0.035 mmol) in dichloromethane (5 mL), which resulted in the immediate formation of a yellow precipitate. The solvent was evaporated, and the residue thus obtained was washed with petroleum ether and dried under reduced pressure to afford the analytically pure product **15** as a yellow solid. Yield: 86% (0.0354 g). Mp: >280 °C. IR (KBr): 3051 (m), 1571 (m), 1510 (s), 1435 (w), 1367 (s), 1260 (w), 1185 (m), 1095 (m), 845 (w), 808 (m), 741 (m), 693 (s), 511 (s) cm^{-1}. CP-MAS ^{31}P NMR δ: −3.6 (s). Anal. Calcd for $C_{114}H_{84}N_6P_6Cu_3I_3$: C, 59.66; H, 3.69; N, 3.66. Found: C, 59.52; H, 3.49; N, 3.58%.

Crystal Structure Determination of Compounds 4, 6, 14, and 15. Single crystal X-ray structural studies of the complexes were performed on a Bruker Smart APEX CCD diffractometer at 100 K. Full spheres of data were collected in three sets of 606 frames (0.3° width in ω) at φ = 0, 120, and 240° under the control of the APEX2[70] program suite. The raw data were reduced to F^2 values using the SAINT[71] software, and global refinements of unit cell parameters using 9767−9925 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS[72]). The structures of **6** and **14** were solved by Patterson methods, while the structures of **4** and **15** were solved by direct methods (SHELXS[73]), and all were refined by full-matrix least-squares procedures (SHELXL[73]). Hydrogen atoms were placed in calculated positions and were included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. All crystals contained disordered lattice solvent, which was removed with the SQUEEZE option of PLATON[74] after attempts to model it proved fruitless. In both compounds **4** and **15**, the molecule has crystallographically imposed 3-fold rotation symmetry, which results in apparent disorder of the phenyl groups, and in these instances, the phenyls were refined as rigid hexagons. Additionally, the latter crystal proved to be a racemic twin. Crystals of **14** rapidly began losing solvent on removal from the mother liquor, and it was only with great difficulty that a reasonably intact crystal could be mounted in the cold stream. Consequently, this structure is of marginal quality, and it is not clear whether the significant residual peaks in the final difference map are the result of the crystal degradation or represent the Pt sites of a minor component of "whole-molecule" disorder. CCDC-950678 2,4,6-C_3N_3{C_6H_4P(S)Ph_2-*p*}$_3$ (**4**), CCDC-950679 [$(AuCl)_3${2,4,6-C_3N_3 ($C_6H_4PPh_2$-*p*)$_3$}] (**6**), CCDC-950680 [$(AuCl)_3${2,4,6-C_3N_3 ($C_6H_4PPh_2$-*p*)$_3$}] (**6a**), CCDC-950677 [$(PtCl_2)_3${2,4,6-C_3N_3 ($C_6H_4PPh_2$-*p*)$_3$}$_2$] (**14**) and CCDC-950681 [$(CuI)_3${2,4,6-C_3N_3 ($C_6H_4PPh_2$-*p*)$_3$}$_2$] (**15**) contain the supplementary crystallographic data for this Paper (see the Supporting Information).

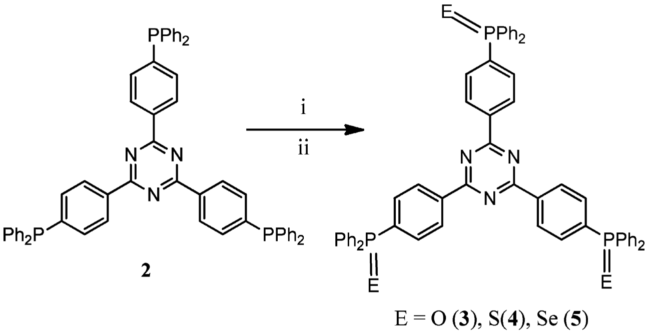
■ RESULTS AND DISCUSSION

Synthesis of 2,4,6-$C_3N_3(C_6H_4PPh_2$-*p*)$_3$ (2). The starting material, 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (**1**) was prepared by the condensation of 4-bromo benzonitrile in the presence of trifluoromethane sulfonic acid according to the reported procedure.[37,75] 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine on treatment with $KPPh_2$ (prepared in situ by the reaction of Ph_2PH and potassium metal in THF) in THF afforded 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine (**2**) in moderate yield (Scheme 1). Earlier attempts to prepare **2** led to the isolation of only tris(phosphineoxide) derivative in 70% yield.[76] The crude product was purified by column chromatography (silica column) using dichloromethane as eluent. Compound **2** is moderately stable to air and moisture in the solid state but readily oxidizes in solution. Substitution of the bromo groups by diphenylphosphine moieties surprisingly enhanced the solubility of the compound in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of **2** showed a singlet at −5.1 ppm. The ^1H NMR spectrum of **2** consists of a doublet at 8.65 ppm, with a $^3J_{HH}$ coupling of 7.6 Hz for the 2′,6′ protons of the phenyl rings attached to the triazine core.

Scheme 1



Scheme 2[a]



[a]Reaction conditions: (i) H_2O_2, THF, RT, 12h. (ii) 3/8 E_8, toluene, reflux 12 h.

Chalcogen Derivatives of Compound 2. To understand the reactivity of phosphorus centers prior to their employment as ligands in coordination chemistry, **2** was interacted with chalcogens. Treatment of **2** with 30% aqueous hydrogen

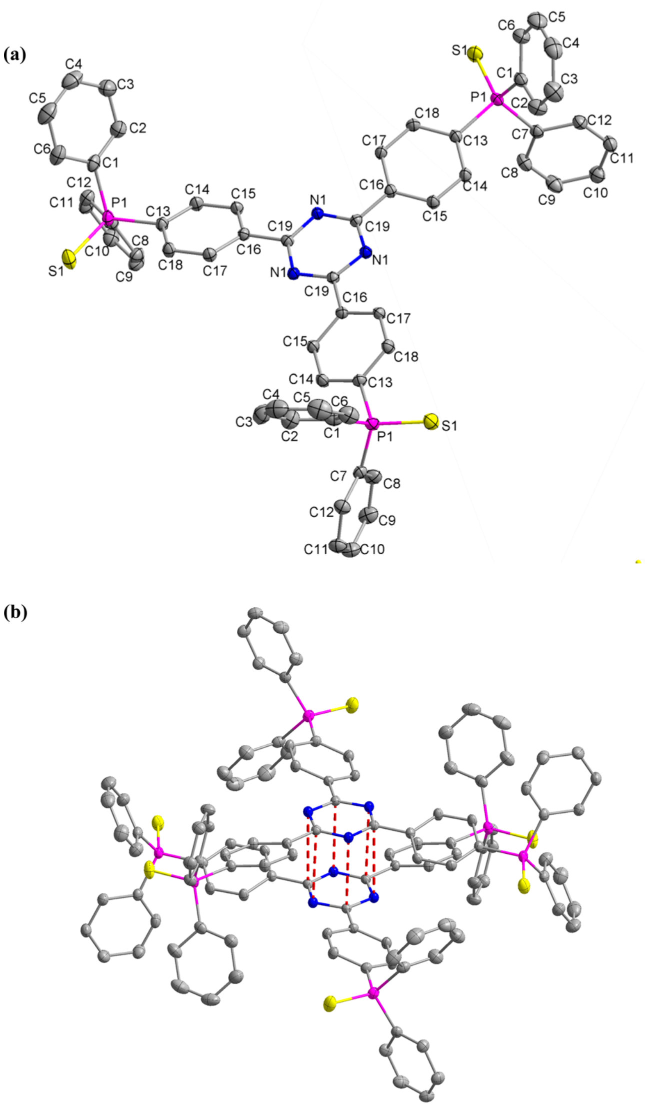


Figure 1. (a) Molecular structure of $C_3N_3\{2,4,6\text{-}C_6H_4P(S)Ph_2\text{-}p\}_3$ (**4**). All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) π-stacked structure of complex **4** with dimeric overlapping.

peroxide in THF yielded the tris(phosphine oxide), 2,4,6-$C_3N_3\{C_6H_4P(O)Ph_2\text{-}p\}_3$ (**3**), while reaction of **2** with elemental sulfur and selenium in toluene under reflux conditions afforded the corresponding trischalcogenides, 2,4,6-$C_3N_3\{C_6H_4P(S)Ph_2\text{-}p\}_3$ (**4**) and 2,4,6-$C_3N_3\{C_6H_4P(Se)Ph_2\text{-}p\}_3$ (**5**), in good yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **3** showed a sharp singlet at 28.9 ppm. The ^1H NMR spectrum displayed a doublet at 8.81 ppm for the 2′,6′ protons of the phenyl rings attached to the triazine core. The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** showed single resonances at 43.1 and 35.1 ppm, respectively, with the latter showing ^{77}Se satellite peaks with a $^1J_{PSe}$ coupling of 736 Hz.

The structure of **4** was determined by X-ray diffraction, using crystals obtained from a solution of **4** in toluene at −10 °C, and a perspective view of the molecular structure is given in Figure 1, with selected bond lengths and bond angles listed in Table 1. In molecule **4**, the central triazine ring and the phenyl groups in the 2, 4, and 6 positions are not coplanar, and the dihedral angles, C15−C16−C19−N1 and C17−C16−C19−N1, are 16.5° and 14.5°, respectively. The average C−N bond distances (~1.343 Å) and the three P−S bond distances are essentially the same (1.9505(10) Å). Interestingly, the structure shows strong intermolecular π−π stacking between the approximately parallel planes of the central triazine rings to form a dimeric structure with an interplane distance of 3.24 Å.[77−79] The observed staggered conformation for the dimer clearly minimizes the steric hindrance between the phosphorus moieties, which allows the triazine rings to approach sufficiently closely to permit the noncovalent π−π interaction to be established.

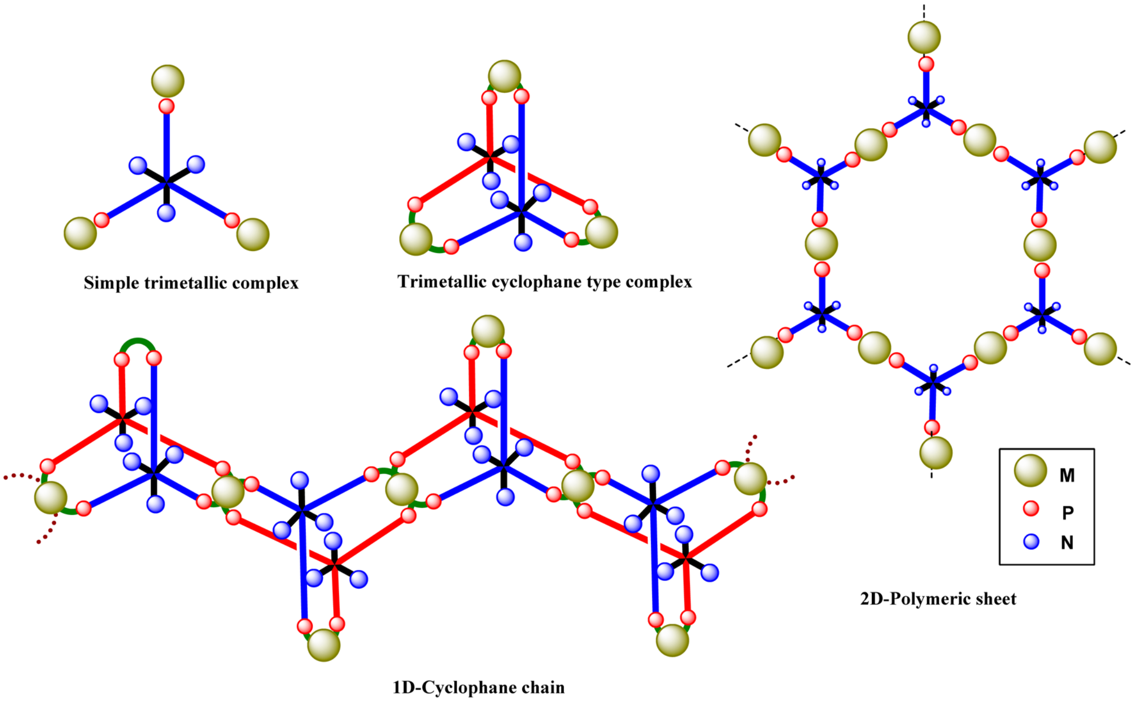
Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 4 and 6

bond distances (Å)		bond angles (deg)	
$C_3N_3\{2,4,6\text{-}C_6H_4P(S)Ph_2\text{-}p\}_3$ (**4**)			
S1−P1	1.9505(10)	S1−P1−C1	113.22(8)
P1−C1	1.818(2)	S1−P1−C7	112.97(8)
P1−C7	1.812(2)	S1−P1−C13	112.30(7)
P1−C13	1.825(2)	C1−P1−C7	106.92(9)
N1−C19	1.336(3)	C1−P1−C13	105.31(10)
N1−C19a	1.343(3)	C7−P1−C13	105.51(10)
$[(AuCl)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**6**)			
Au1−P1	2.2293(15)	Cl1−Au1−P1	177.45(6)
Au2−P2	2.2340(14)	Cl2−Au2−P2	177.16(5)
Au3−P3	2.2282(15)	Cl3−Au3−P3	175.28(6)
Au1−Cl1	2.2819(19)	Au1−P1−C7	113.84(17)
Au2−Cl2	2.2879(15)	Au1−P1−C10	112.91(19)
Au3−Cl3	2.2766(16)	Au1−P1−C16	113.20(19)
N1−C2	1.320(7)	Au2−P2−C25	112.3(2)
N1−C3	1.333(7)	Au2−P2−C28	113.7(2)
N2−C1	1.339(7)	Au2−P2−C34	112.6(2)
N2−C2	1.344(7)	Au3−P3−C43	113.3(2)
N3−C1	1.358(7)	Au3−P3−C46	115.0(2)
N3−C3	1.337(6)	Au3−P3−C52	111.2(2)
P1−C7	1.813(5)	C2−N1−C3	114.6(4)
P2−C25	1.823(6)	C1−N2−C2	114.5(4)
P3−C43	1.821(6)	C1−N3−C3	114.1(4)
		N1−C2−N2	126.1(5)
		N1−C3−N3	126.0(5)
		N2−C1−N3	124.7(5)

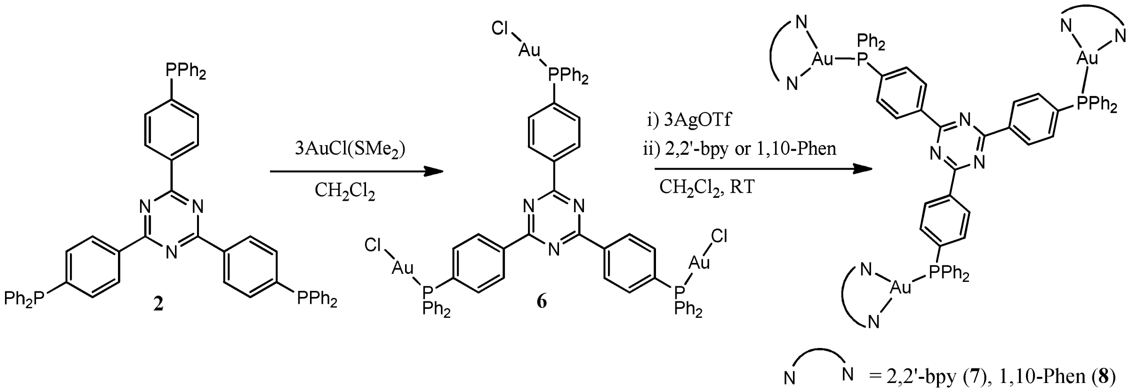
Transition Metal Chemistry. Similar to the trispyridyl ligand **I**, the trisphosphine **2** is a potential tridentate ligand, but the donor phosphorus(III) arms are more flexible due to the free rotation of phosphorus centers about the *ipso*-carbon atom making it more accommodative in terms of its coordinating features. Hence it would be interesting to explore its coordination behavior with various transition metal salts. The possible coordinating modes of trisphosphine **2** are depicted in Chart 2.

The reaction of **2** with $[AuCl(SMe_2)]$ in a 1:3 molar ratio in dichloromethane produced a white crystalline trinuclear complex, $[(AuCl)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**6**). The $^{31}P\{^1H\}$ NMR spectrum of complex **6** exhibits a single resonance at 33.0 ppm. The synthesis of trisgold complex containing the analogous phenyl derivative 1,3,5-tris[4-(diphenylphosphino)phenyl]benzene has been reported.[59] The gold complex **6** on treatment with 3 equiv of AgOTf, followed by the addition of 2,2′-bpy or 1,10-phen gave the corresponding substituted complexes, $[\{Au(2,2'\text{-}bpy)\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}](OTf)_3$ (**7**) and $[\{Au(1,10\text{-}phen)\}_3\{2,4,6\text{-}C_3N_3\text{-}(C_6H_4PPh_2\text{-}p)_3\}](OTf)_3$ (**8**) as white crystalline solids (Scheme 3). These complexes are insoluble in most of

Chart 2. Possible Coordinating Modes of Triazene-Based Trisphosphines



Scheme 3



the common organic solvents except dimethyl sulfoxide (DMSO). The $^{31}P\{^1H\}$ NMR spectra of complexes **7** and **8** exhibit single resonances at 35.7 and 35.8 ppm, respectively.

Crystals of **6** suitable for X-ray diffraction study were obtained by slow diffusion of petroleum ether into a dichloromethane solution of the complex, from which two different types of crystals, **6** and **6a**, were obtained. The structures are presented in Figure 2, and selected bond parameters are listed in Table 2. From the molecular structure of **6** it is clear that the molecule is not planar as indicated from the dihedral angle between the plane of the triazine ring and the phenyl rings [23.09(1)° for C4−C5−C6, 15.01(1)° for C22−C23−C24, and 11.49(1)° for C40−C41−C42]. The C−N bond lengths of the triazine ring are not identical as the C1−N3 (1.358(7) Å) bond is slightly longer than the others [C−N ≤ 1.34 Å] although the difference is barely significant. The three P−Au−Cl groups display normal bond distances, with two of these [those involving Au(1) and Au(2)] protruding away from the plane of the triazine ring while the third one, Au(3), is coplanar with it. The average P−Au−Cl bond angle of 176.7° indicates a slight deviation from linear geometry around the Au atoms. The shortest intermolecular Au···Au distance is 4.28 Å, which is considerably longer than the sum of their van der Waals radii (3.41 Å), indicating the absence of any aurophilic interactions. Similar to compound **4**, in compound **6** the molecules also appear in pairs, with a distance of ca. 3.24 Å between the mean planes of the triazine rings. However, here the centroids of the two triazine rings exhibit a parallel displacement of approximately 2.40 Å such that the centroid of one ring lies over the center of the line from N1 to C45. This places the edges of the upper ring over the N1−C8−C40−C45 portion of the lower molecule. This could indicate intermolecular $\pi-\pi$ stacking, but it would necessarily be of the "slipped" variety.

The molecular structure of the second crystalline form obtained for **6** (**6a**) reveals that both Au2 and Au3 are involved in intermolecular aurophilic interactions with short Au···Au contacts of 3.0600(6) Å leading to a one-dimensional polymeric chain structure as shown in Figure 2c. Analogously to the structure of **6**, the molecular structure of **6a** shows

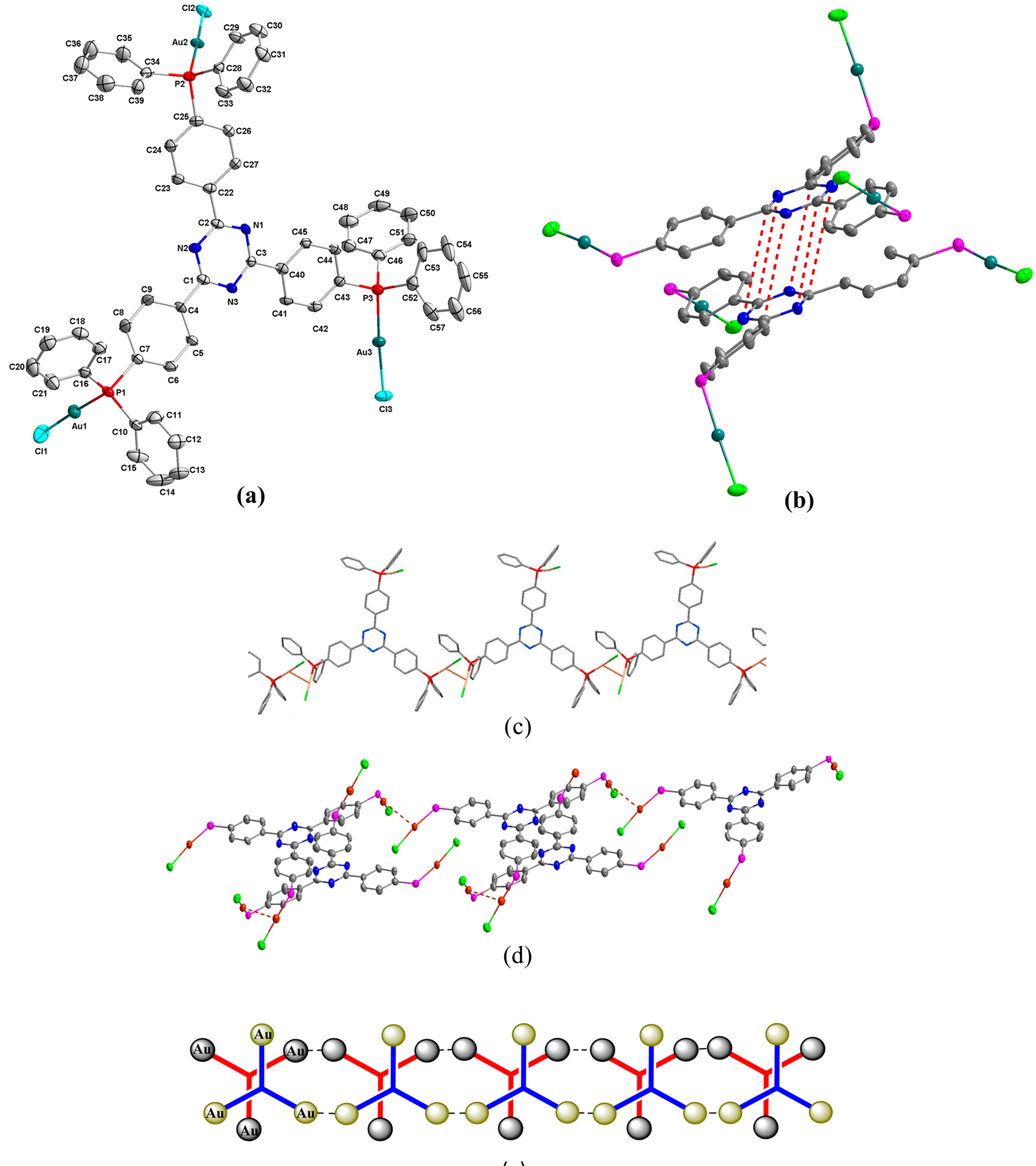


Figure 2. (a) Molecular structure of $[(AuCl)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**6**). All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) π-Stacking in $[(AuCl)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**6**). (c) Intermolecular Au···Au interactions in **6a** leading to a 1D chain structure. (d) Weak π-stacking in **6a** due to the packing in staggered fashion. (e) A cartoon showing the arrangement of chains viewed down on the triazine plane. For **6a**: bond distances (Å): Au1—Cl1, 2.283(4); Au1—P1, 2.218(4); Au2—Cl2, 2.304(3), Au2—P2, 2.232(3), Au3—Cl3, 2.311(3), Au3—P3, 2.230(3); averg. N−C, 1.339(17); averg. P−C, 1.816(14). Bond angles (deg): Cl1—Au1—P1, 173.63(15); Cl2—Au2—P2, 172.26(13); Cl3—Au3—P3, 177.13(13).

intermolecular slipped π−π stacking, but the formation of the polymeric chain results in an increase of the interplane distance from 3.24 Å to 3.50 Å, which weakens the π−π interaction. Because of the intermolecular π−π interaction, the two layers of molecules orient in such a way that the free P1−Au1−Cl1 unit of one layer comes in close contact with the P3−Au3−Cl3 unit of the other layer with a short Au···Au contact of 3.40 Å, which is slightly shorter than the sum of their van der Waals radii (3.41 Å) and so is not considered a significant aurophilic interaction.

The reaction of **2** with 1.5 equiv of $[Ru(\eta^6\text{-cymene})Cl_2]_2$ or $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ resulted in the formation of $[\{Ru(\eta^6\text{-cymene})Cl_2\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**9**) and $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**10**) in good yield.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 14 and 15

bond distances (Å)		bond angles (deg)	
$[(PtCl_2)_3\{C_3N_3\{2,4,6\text{-}C_6H_4PPh_2\text{-}p\}_3\}_2]$ (**14**)			
Pt1−P1	2.254(3)	Cl1−Pt1−Cl2	88.98(11)
Pt1−P2	2.259(3)	Cl1−Pt1−P1	84.49(10)
Pt2−P3	2.247(3)	Cl2−Pt1−P2	82.07(11)
Pt2−P3a	2.247(3)	P1−Pt1−P2	104.47(10)
Pt1−Cl1	2.337(3)	Cl3−Pt2−P3	82.57(10)
Pt1−Cl2	2.362(3)	Cl3−Pt2−Cl3a	88.75(11)
Pt2−Cl3	2.341(3)	P3−Pt2−P3a	106.29(9)
Pt2−Cl3a	2.341(3)		
$[(CuI)_3\{C_3N_3\{2,4,6\text{-}C_6H_4PPh_2\text{-}p\}_3\}_2]$ (**15**)			
I1−Cu1	2.582(10)	I1−Cu1−P1	105.0(3)
Cu1−P2	2.187(9)	P1−Cu1−P2	125.0(5)
Cu1−P1	2.331(9)	I1−Cu1−P2	120.3(4)
P1−C1	1.898(19)	Cu1−P1−C33	106.4(5)
P2−C14	1.760(15)	C1−P1−C8	102.3(8)
		Cu1−P1−C1	112.2(5)

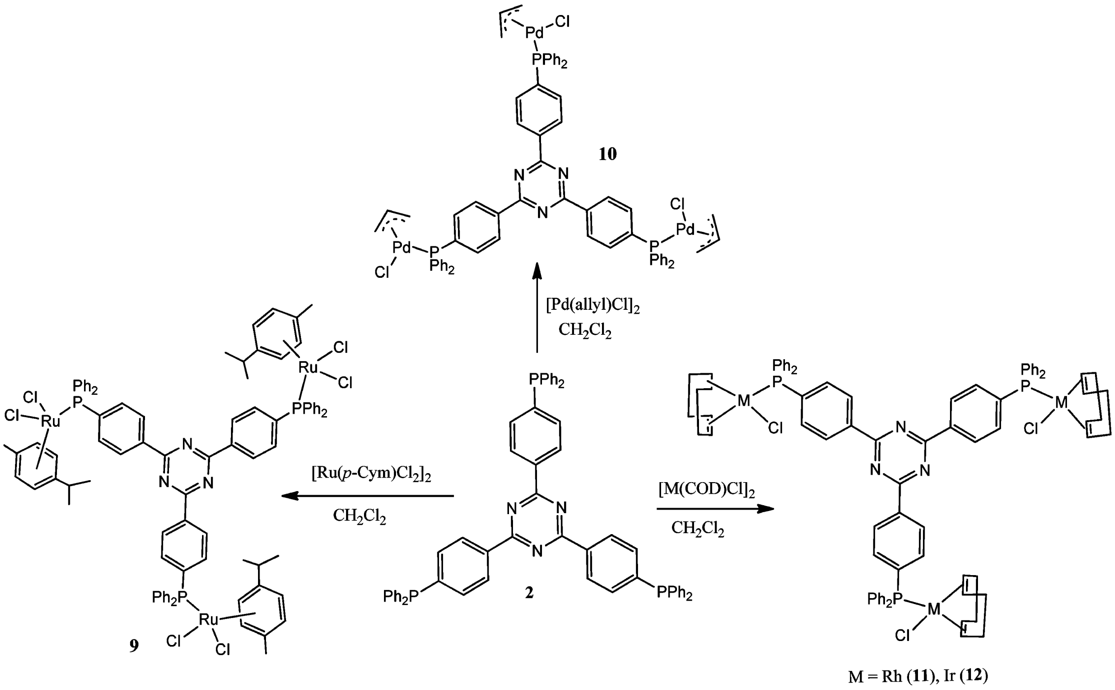
The $^{31}P\{^1H\}$ NMR spectrum of **9** shows a single resonance at 24.7 ppm. The presence of the coordinated cymene group was confirmed by the ^1H NMR spectrum, which shows a singlet at 1.9 ppm corresponding to the methyl protons, whereas those of isopropyl groups show doublets at 1.11 ppm and a septet at 2.87 ppm with a $^3J_{HH}$ coupling of 6.8 Hz. The four aromatic protons of the cymene groups show two doublets at 5.03 and 5.23 ppm. Complex **10** shows a single resonance at 22.8 ppm in its $^{31}P\{^1H\}$ NMR spectrum.

The reaction of **2** with 1.5 equiv of $[M(COD)Cl]_2$ (M = Rh or Ir) in dichloromethane afforded trinuclear complexes $[\{Rh(COD)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**11**) and $[\{Ir(COD)Cl\}_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}]$ (**12**), respectively, as shown in Scheme 4. The $^{31}P\{^1H\}$ NMR spectrum of complex **11** consists of a doublet centered at 30.9 ppm with a $^1J_{RhP}$ coupling of 150.6 Hz, whereas that of **12** shows a singlet at 22.1 ppm. The ^1H NMR spectra of complexes **11** and **12** showed broad singlets at 5.62 ppm and 5.24 ppm, respectively, for the olefinic protons of COD. The methylenic protons present in complexes **11** and **12** exhibit two multiplets at 2.06, 2.43 ppm and 1.61, 2.28 ppm, respectively.

The reaction of **2** with $[M(COD)Cl_2]$ (M = Pd or Pt) in a 2:3 molar ratio in dichloromethane afforded colorless crystalline metallocyclophane complexes of the type $[(MCl_2)_3L_2]$ (M = Pd, **13**; Pt, **14**) (L = 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine). Complex **13** is insoluble in most of common solvents, whereas **14** is sparingly soluble only in DMSO. Because of the negligible solubility of these complexes in most common organic solvents the spectroscopic characterization is not satisfactory. However, the ^{31}P CP-MAS spectrum of **13** showed a broad single resonance at 24.8 ppm, which is comparable with the same observed for *cis*-$[PdCl_2(PPh_3)_2]$ (23.5 ppm).[80] Balch and co-workers have reported similar metallocyclophanes of palladium and platinum derived from 1,3,5-tris(diphenylphosphino)-benzene, but because of the insolubility of the complex, they have not carried out the spectroscopic studies.[81] However, the $^{31}P\{^1H\}$ NMR spectrum of **14** showed a broad singlet at 13.5 ppm with a $^1J_{PtP}$ coupling of 3734 Hz, which is comparable with that of simple complex, *cis*-$[Pt(PPh_3)_2Cl_2]$.[82−84] The ^{31}P CP-MAS spectra of **14** also showed a single resonance at 16.1 ppm with a $^1J_{PtP}$ coupling of 3719 Hz. This slight discrepancy is not unusual as there will be some shift in the solid state spectra. For example, the solution ^{31}P NMR spectrum of *cis*-$[PtCl_2(PPh_3)_2]$ showed a single resonance at 14.7 ppm ($^1J_{PtP}$ = 3681 Hz), whereas its CP-MAS spectrum consists of a broad resonance at 12.9 ppm with a $^1J_{PtP}$ coupling of 3877 Hz.[85]

The reaction of **2** with CuI in a 2:3 molar ratio in dry acetonitrile afforded a cyclophane $[(CuI)_3L_2]$ (**15**) similar to **14**. The complex **15** is insoluble in common organic solvents and as a result spectroscopic characterization could not be

Scheme 4



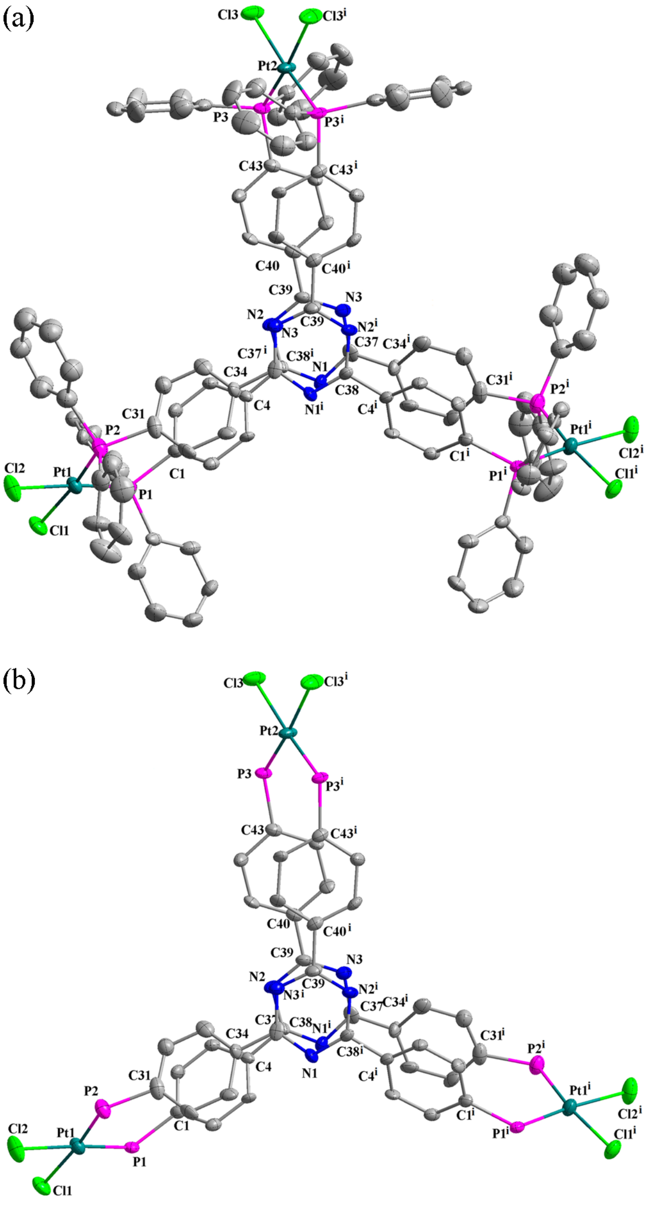


Figure 3. (a) Molecular structure of $[(PtCl_2)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}_2]$ (**14**). All hydrogen atoms are removed for clarity. (b) Skeletal structure of **14**.

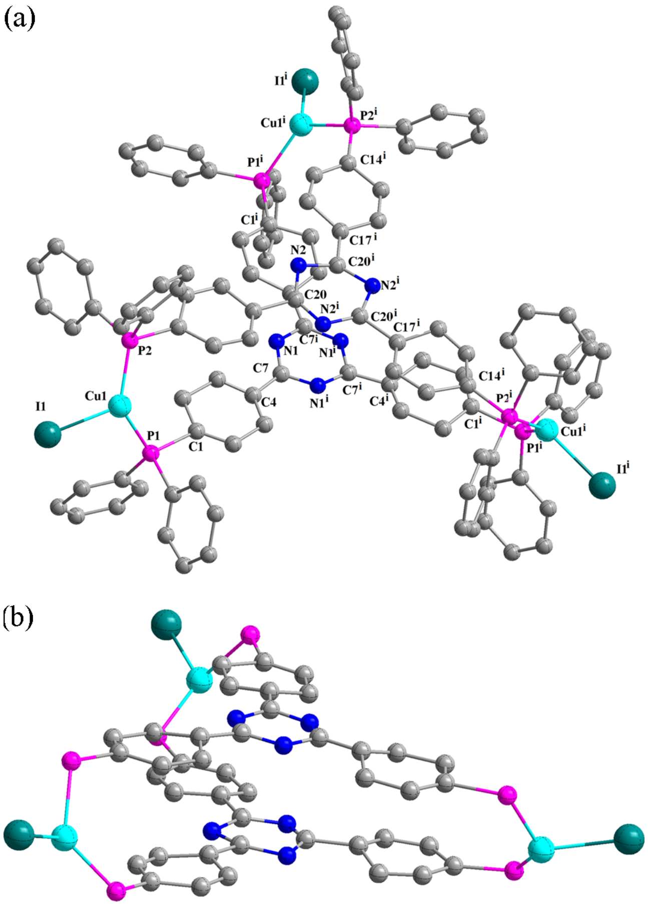
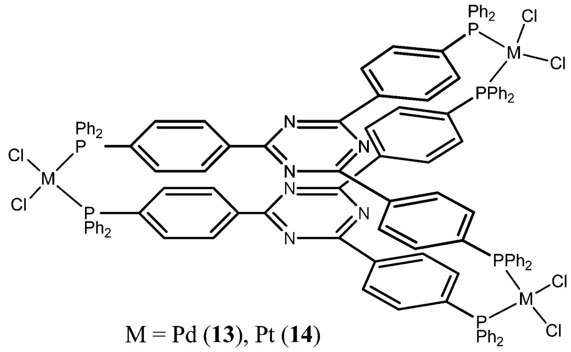
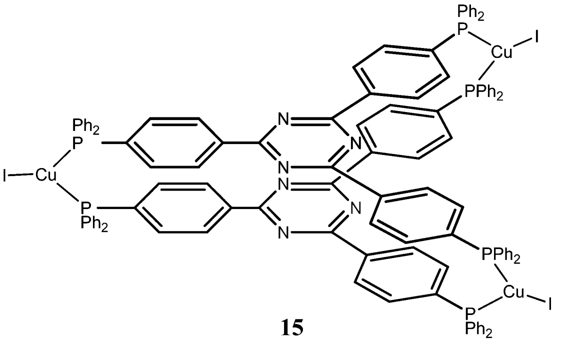


Figure 4. (a) Molecular structure of $[(CuI)_3\{2,4,6\text{-}C_3N_3(C_6H_4PPh_2\text{-}p)_3\}_2]$ (**15**). All hydrogen atoms are removed for clarity. (b) Skeletal structure of complex **15**.

carried out. However, the molecular structure is confirmed from the elemental analysis, ^{31}P CP-MAS, powder and single crystal X-ray diffraction study. ^{31}P CP-MAS spectrum of **15** showed a broad signal at −3.3 ppm which is similar to the same observed in the case of $[CuI(PPh_3)_2]$ (−3.6 ppm).[86] The powder diffraction of complex **15** is similar to the pattern simulated from its single crystal X-ray data.



M = Pd (**13**), Pt (**14**)



15

The structures of **14** and **15** were determined by X-ray diffraction methods and are shown in Figures 3 and 4, with relevant bond distances and angles listed in Table 2. Since the platinum and copper metallocyclophanes **14** and **15** are highly insoluble in most of the organic solvents, they were synthesized through crystallization by solvent-diffusion methods. An

Table 3. Crystallographic Information for Complexes **4**, **6**, **6a**, **14**, and **15**

	4	**6**	**6a**	**14**	**15**
emp. formula	$C_{57}H_{42}N_3P_3S_33(C_7H_8)$	$C_{57}H_{42}Au_3Cl_3N_3P_3$	$C_{57}H_{42}Au_3Cl_3N_3P_3$	$C_{114}H_{84}Cl_6N_6P_6Pt_3$	$C_{114}H_{84}Cu_3I_3N_6P_6$
formula wt	1234.43	1559.10	1559.10	2521.66	2295.01
cryst. system	trigonal	triclinic	triclinic	monoclinic	trigonal
space group	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$R3c$ (No. 161)
a, Å	19.274(5)	11.3827(8)	12.5403(12)	34.660(6)	20.302(2)
b, Å	19.274(5)	14.314(1)	13.7369(13)	19.562(4)	20.302(2)
c, Å	31.844(8)	19.9079(14)	16.9325(17)	20.249(4)	46.497(5)
α, deg	90	106.484(1)	88.724(1)	90	90
β, deg	90	104.102(1)	88.473(1)	123.357(2)	90
γ, deg	120	90.936(1)	84.990(1)	90	120
V, Å^3	10245(4)	3003.8(4)	2904.1(5)	11468(4)	16597.1(17)
Z	6	2	2	4	6
$D_{calc,}$ g cm^{-3}	1.201	1.724	1.783	1.461	1.378
μ (Mo Kα), mm^{-1}	0.224	7.557	7.817	3.921	1.543
F (000)	3888	1476	1476	4944	6876
T (K)	100	100	100	100	100
θ range, deg	1.4−27.4	1.9−28.3	1.5−27.1	1.3−25.8	2.0−23.3
total no. reflns	29541	52016	23997	41889	32749
no. of indep reflns	5169 [R_{int} = 0.060]	14603 [R_{int} = 0.060]	12453 [R_{int} = 0.060]	10923 [R_{int} = 0.071]	5306 [R_{int} = 0.071]
S	1.08	1.01	0.97	1.07	1.10
R_1	0.0493	0.0380	0.0643	0.0702	0.0758
wR_2	0.1420	0.0919	0.1684	0.2080	0.2288

acetonitrile solution of [Pt(COD)Cl_2] or CuI was allowed to diffuse slowly into a dichloromethane solution of the ligand 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine over a period of 2 h through the walls of the round-bottom flask using a very thin capillary tube, and the resulting clear solution was kept undisturbed for 24 h to get X-ray quality crystals. The molecules of **14** crystallized in a monoclinic crystal system with centro-symmetric space group ($C2/c$). The molecule consists of two trisphosphines held together by three $PtCl_2$ groups as straps, with distorted square-planar geometry around the platinum metals. The separation between the two triazine rings is 3.512 Å, which is longer than the corresponding distance in purely organic paracyclophane (3.25 Å)[87] and in the analogous complex [$(PtCl_2)_3L_2$] (3.12 Å).[81] The P···P separations (P1−P2A = P2−P1A = 3.570(5) Å and P3−P3A = 3.598(5) Å) are longer than the center-to-center triazine ring separation. The closer contact between the triazine rings is due to noncovalent $\pi \cdots \pi$ interactions. The bridging phenyl groups and the triazine ring are not coplanar.

The bonding pattern in complex **15** is similar to that of complex **14** with distorted trigonal-planar geometry around the copper centers. The separation between the two triazine rings (3.371 Å) is smaller than it is in the platinum complex **14**. Complex **15** has crystallographically imposed C_3 rotation symmetry, with the unique bridging phenylene group coplanar with the triazine ring. The unique P···P distance (4.008 Å) is longer than those in complex **14**. Crystallographic information for complexes **4**, **6**, **6a**, **14**, and **15** is given in Table 3.

CONCLUSIONS

In summary, we are reporting for the first time a triazine-bound trisphosphine 2,4,6-tris{4-(diphenylphosphino)phenyl}-1,3,5-triazine (**2**), synthesized by treating $KPPh_2$ with 2,4,6-tris(4-bromophenyl)-1,3,5-triazine. Interestingly, substitution of the bromo group by diphenylphosphine enhanced the solubility of **2** compared to 2,4,6-tris(4-bromophenyl)-1,3,5-triazine. The trisphosphine **2** serves as a potential rigid tridentate ligand capable of forming simple trimetallic complexes, 1D polymers, and also cyclophane-type complexes. The presence of the triazine core favors noncovalent $\pi - \pi$ interactions. The triazine nitrogen atoms in metallocyclophanes with eclipsed conformation can further facilitate the second-tier cyclophane formation with platinum metals or can sandwich anions. Work in this direction is in progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic structural information for compounds **4**, **6**, **6a**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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