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Synthesis, spectral and molecular studies of half-sandwich arene ruthenium and Cp*Rh/Cp*Ir complexes containing bidentate P-N and E-N ligands (E = S, Se) based on diphenyl(2-pyridyl)phosphine

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The chalcogenide ligands {E=PPh₂Py} (E = O, S, Se) were prepared by direct oxidation of diphenyl(2-pyridyl)phosphine using H₂O₂, S and Se powder, respectively. The reaction of ligand with starting metal precursors [(arene)RuCl₂]₂ {M = Ru, arene = benzene; *p*-cymene} and [Cp*MCl₂]₂ (M = Rh, Ir) afforded a series of cationic half sandwich complexes, [(arene/Cp*)MCl{κ²-(NE)-EPPH₂Py}]⁺. Reaction of O=PPh₂Py with precursors yielded known complexes [(arene/Cp*)MCl{κ²-(PN)-PPh₂Py}]⁺ instead of expected complexes [(arene/Cp*)MCl{κ²-(NO)-O=PPh₂Py}]⁺. All new complexes were isolated as PF₆⁻ counterion and characterized by spectroscopic techniques like FT-IR, NMR, mass, UV-Vis. Some representative complexes were structurally determined by X-ray crystallographic analysis, revealing typical three-legged piano stool geometry around the metal center with a five-membered metallacycle.

Keywords: Arene ligands; Ruthenium; Rhodium; Iridium; Diphenyl(2-pyridyl)phosphine ligands

1. Introduction

The heterobidentate P, N-donor diphenyl(2-pyridyl)phosphine (PPh₂Py) represents an important class of hemilabile ligands which binds to metal with medium strength. Metal complexes containing hemilabile ligands provided a potential site for the reversible binding to metal center because of their dynamic chelating ability. Owing to their ability to reversibly bind, hemilabile metal complexes are extremely important in catalysis and have been used in various organic transformations [1-3].

Organophosphine ligands having S or Se donors receive attention due to their catalytic properties [4, 5]. A number of transition metal complexes containing functionalized P-X (X = chalcogen donors) ligands have been reported. We became interested in the study of E=PPh₂Py as potentially hemilabile ligands and their catalytic studies. For example rhodium and ruthenium carbonyl complexes of functionalized phosphine chalcogen donors, P-X (X = O, S, Se), have been studied in catalytic applications particularly in carbonylation of alcohols, hydrogenation of unsaturated substrates and hydroformylation of alkenes for industrially important organic molecules [6-10].

Our group has been interested in the synthesis of arene ruthenium and Cp*Rh/Cp*Ir complexes with various mono/bidentate ligands containing nitrogen donors. Recently, we reported the synthesis of neutral and

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cationic half-sandwich platinum group complexes with diphenyl(2-pyridyl)phosphine [11-13]. However, arene ruthenium and Cp*Rh/Cp*Ir complexes with chalcogenide, E=PPh₂Py (E = S, Se), have not been explored. As a part of our continuing study, we would like to report syntheses of a series of new mononuclear half sandwich complexes of arene Ru(II), Cp*Rh(III) and Cp*Ir(III) with bidentate phosphine chalcogenide ligands.

2. Experimental

2.1. Physical methods and materials

All the experiments were performed under normal conditions. All reagents were purchased from commercial sources and used as received. RuCl₃·nH₂O, RhCl₃·nH₂O and IrCl₃·nH₂O were purchased from Arora Matthey limited, diphenyl(2-pyridyl)phosphine was obtained from Aldrich, sulfur and selenium powder were acquired from Merck. The solvents were purified and dried according to standard procedures [14]. The starting metal precursors [(benzene)RuCl₂]₂, [(p-cymene)RuCl₂]₂ and [Cp*MCl₂]₂ (M = Rh or Ir) [15], chalcogenide E=PPh₂Py were prepared by modified literature methods [5]. NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 2400 CH/N analyzer. Mass spectra were obtained using a Waters ZQ 4000 mass spectrometer by the ESI method in positive mode. Absorption spectra were obtained at room temperature using a Perkin-Elmer Lambda 25 UV/visible spectrophotometer.

2.2. Single-crystal X-ray structures analyses

Orange or yellow crystals of **2**, **6-9** and **12** were obtained by slow diffusion of hexane into acetone solution of the corresponding complexes. Single crystal X-ray diffraction measurements were carried out on an Oxford Diffraction Xcalibur Eos Gemini diffractometer. Crystal data were collected at 300 K using graphite monochromated Mo K α radiation (λ = 0.71073 Å). The strategy for data collection was evaluated using the CrysAlisPro CCD software. Crystal data were collected by standard “phi-omega scan” techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97 refining on F² [16, 17]. The positions of all atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 Ueq of their parent atoms. Crystallographic details are summarized in table 1 and selected bond lengths and angles are presented in table 2. Figures 1-3 were drawn with ORTEP-3 and figure 4 was drawn with MERCURY [18].

2.3. Syntheses of metal complexes (1-8)

Mixture of the metal precursor [(arene)RuCl₂]₂ or [Cp*MCl₂]₂ (0.1 mmol) and E=PPh₂Py (E = S, Se) (0.2 mmol) was dissolved in methanol (20 ml) then stirred at room temperature for 6 h. A yellow or orange precipitate formed immediately after adding NH₄PF₆ (2 molar equivalents) to the reaction mixture. The precipitate was washed with methanol (5 ml), diethyl ether (3×10 ml) and dried under vacuum.

2.3.1. [(benzene)Ru(S=PPh₂Py)Cl]PF₆ (1). Color: Orange precipitate; Yield: 50 mg (77%); IR (KBr, cm⁻¹): 3449(b), 3090(m), 1628(w), 1587(m), 1481(w), 1451(m), 1437(s), 1383(m), 1335(w), 1309(m), 1286(w),

1187(m), 1131(w), 1102(s), 1023(m), 993(w), 840(vs), 766(s), 742(s), 711(m), 693(s), 558(s), 525(s), 510(s); ^1H NMR (400 MHz, CD_3CN): δ = 9.20 (d, 1H, H_{JJ} = 3.25, py ring), 7.84 (t, 1H, py ring), 7.71-7.61 (m, 3H, py & ph ring), 7.58-7.54 (m, 4H, ph ring), 7.38-7.30 (m, 4H, ph ring), 7.15 (t, 1H, py ring), 5.31 (s, 6H, benzene ring); ^{13}C NMR (400 MHz, CD_3CN): δ = 160.28, 154.53, 139.61, 134.71, 132.91, 132.01, 130.74, 129.82, 128.69, 86.20; ESI-MS: 509.90 [M^+] peak, 475.03 [$\text{M}^+ - \text{Cl}$] peak, 214.89 [(ben)RuCl $^+$] peak; UV-Vis { CH_3CN , λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 226(5800), 330(500); Anal. Calc. for $\text{C}_{23}\text{H}_{20}\text{NSRuClPF}_6$ (654.96) (%): C, 42.18; H, 3.08; N, 2.12. Found (%): C, 42.50; H, 3.22; N, 2.20.

2.3.2. [(p-cymene)Ru(S=PPh $_2$ P)Cl]PF $_6$ (2). Color: Orange precipitate; Yield: 57 mg (80%); IR (KBr, cm^{-1}): 3449(b), 3080(m), 2969(m), 1629(w), 1587(m), 1483(m), 1437(s), 1383(w), 1333(w), 1283(m), 1129(w), 1101(s), 1058(m), 1028(w), 998(m), 839(vs), 768(s), 741(s), 710(s), 693(s), 557(vs), 525(s), 509(s); ^1H NMR (400 MHz, CD_3CN): δ = 9.38 (d, 1H, H_{JJ} = 3.25, py ring), 8.10 (t, 1H, py ring), 7.98-7.92 (m, 3H, py & ph ring), 7.81-7.77 (m, 4H, ph ring), 7.62-7.51 (m, 4H, ph ring), 5.86 (d, 2H, H_{JJ} = 3.75, ph ring), 5.63 (d, 2H, H_{JJ} = 3.75, ph ring), 2.70 (sep, 1H, Ar(p -Cy)), 2.48 (s, 3H, CH_3), 1.99 (s, 3H, $\text{CH}_3\text{Ar}(\text{p-Cy})$), 1.32 (d, 6H, H_{JJ} = 4.00, $\text{CH}_3\text{Ar}(\text{p-Cy})$), 1.21 (d, 6H, H_{JJ} = 4.25, $\text{CH}_3\text{Ar}(\text{p-Cy})$); ^{13}C NMR (400 MHz, CD_3CN): δ = 159.64, 154.55, 139.71, 134.68, 132.85, 132.10, 130.78, 129.87, 129.02, 103.16, 90.59, 85.04, 83.67, 30.49, 21.76, 16.98; ESI-MS: 566.10 [M^+] peak, 531.01 [$\text{M}^+ - \text{Cl}$] peak, 236.05 [(p-cy)RuCl $^+$] peak; UV-Vis { CH_3CN , λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 229(6600), 335(600); Anal. Calc. for $\text{C}_{27}\text{H}_{28}\text{NSRuClPF}_6$ (711.04) (%): C, 45.61; H, 3.97; N, 1.97. Found (%): C, 45.73; H, 4.17; N, 2.10.

2.3.3. [Cp * Rh(S=PPh $_2$ Py)Cl]PF $_6$ (3). Color: Red orange precipitate; Yield: 56 mg (79%); IR (KBr, cm^{-1}): 3133(b), 1619(w), 1585(m), 1437(m), 1401(s), 1312(w), 1279(m), 1185(w), 1159(m), 1131(m), 1101(s), 1019(s), 998(m), 840(vs), 766(s), 709(s), 693(s), 622(m), 606(s), 558(vs), 525(s), 504(s); ^1H NMR (400 MHz, CD_3CN): δ = 9.02 (d, 1H, H_{JJ} = 3.25, py ring), 8.12 (t, 1H, py ring), 7.88 (d, 2H, H_{JJ} = 2.00, ph ring), 7.79-7.74 (m, 5H, ph ring), 7.60-7.55 (m, 4H, ph ring), 7.43 (t, 1H, py ring), 1.44 (s, 15H, Cp * ring); ^{13}C NMR (400 MHz, CD_3CN): δ = 156.73, 153.79, 139.67, 134.16, 132.54, 132.11, 131.32, 129.39, 126.12, 97.63, 7.85; ESI-MS: 568.00 [M^+] peak, 532.05 [$\text{M}^+ - \text{Cl}$] peak, 236.05 [Cp * RhCl $^+$] peak; UV-Vis { CH_3CN , λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 243(3100), 402(300); Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{NSRhClPF}_6$ (714.90) (%): C, 45.36; H, 4.23; N, 1.96. Found (%): C, 45.50; H, 4.42; N, 2.13.

2.3.4. [Cp * Ir(S=PPh $_2$ Py)Cl]PF $_6$ (4). Color: Yellow precipitate; Yield: 61 mg (75%); IR (KBr, cm^{-1}): 3436(b), 3094(w), 2994(w), 2925(w), 1585(w), 1455(w), 1439(m), 1384(m), 1313(w), 1187(w), 1136(m), 1100(s), 1027(s), 999(w), 862(s), 841(vs), 781(m), 756(m), 710(m), 626(m), 607(m), 558(s), 523(s), 516(s); ^1H NMR (400 MHz, CD_3CN): 9.14 (d, 1H, H_{JJ} = 3.25, py ring), 8.09 (t, 1H, py ring), 7.84 (d, 2H, H_{JJ} = 2.00, ph ring), 7.67-7.60 (m, 5H, ph ring), 7.56-7.50 (m, 4H, ph ring), 7.39 (t, 1H, py ring), 1.46 (s, 15H, Cp * ring); ^{13}C NMR (400 MHz, CD_3CN): δ = 157.82, 154.25, 139.78, 134.38, 132.91, 132.48, 131.79, 129.65, 126.43, 97.65, 8.35; ESI-MS: 658.09 [M^+] peak, 622.10 [$\text{M}^+ - \text{Cl}$] peak, 363.02 [Cp * IrCl $^+$] peak; UV-Vis { CH_3CN , λ_{max} nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 226(10000), 314(2400), 375(900); Anal. Calc. for $\text{C}_{27}\text{H}_{30}\text{NSIrClPF}_6$ (804.21) (%): C, 40.32; H, 3.76; N, 1.74. Found (%): C, 40.51; H, 3.87; N, 1.91.

2.3.5. [(benzene)Ru(Se=PPh₂Py)Cl]PF₆ (5). Color: Orange precipitate; Yield: 53 mg (75%); IR (KBr, cm⁻¹): 3431(b), 3133(w), 1637(m), 1587(m), 1479(w), 1436(m), 1400(vs), 1314(w), 1286(m), 1186(w), 1141(m), 1096(s), 1000(w), 836(vs), 771(m), 754(m), 716(m), 688(m), 616(w), 557(vs), 510(s); ¹H NMR (400 MHz, CD₃CN): δ = 9.10 (d, 1H, H_{JJ} = 3.25, py ring), 8.20 (t, 1H, py ring), 7.92 (d, 2H, H_{JJ} = 2.00, ph ring), 7.80-7.75 (m, 5H, ph ring), 7.63-7.57 (m, 4H, ph ring), 7.41 (t, 1H, py ring), 5.60 (s, 6H, benzene ring); ¹³C NMR (400 MHz, CD₃CN): δ = 162.54, 152.20, 136.26, 135.42, 132.67, 131.87, 130.42, 128.62, 126.71, 85.90; ESI-MS: 557.89 [M⁺] peak, 522.90 [M⁺-Cl] peak, 214.90 [(ben)RuCl⁺] peak; UV-Vis {CH₃CN, λ_{max} nm (ε, M⁻¹ cm⁻¹)}: 228(7300), 324(700); Anal. Calc. for C₂₃H₂₀NSeRuClPF₆ (701.83) (%): C, 39.36; H, 2.87; N, 2.00. Found (%): C, 39.53; H, 2.99; N, 2.17.

2.3.6. [(p-cymene)Ru(Se=PPh₂Py)Cl]PF₆ (6). Color: Orange precipitate; Yield: 59 mg (78%); IR (KBr, cm⁻¹): 3434(m), 3129(m), 2970(m), 1631(m), 1584(w), 1456(m), 1439(s), 1400(s), 1320(m), 1280(w), 1186(w), 1133(m), 1100(s), 1054(m), 1028(w), 838(vs), 779(w), 756(w), 693(m), 557(vs), 518(s); ¹H NMR (400 MHz, CD₃CN): δ = 9.15 (d, 1H, H_{JJ} = 3.25, py ring), 8.21 (t, 1H, py ring), 7.80 (d, 2H, H_{JJ} = 2.25, ph ring), 7.76-7.71 (m, 5H, ph ring), 7.61-7.55 (m, 4H, ph ring), 7.42 (t, 1H, py ring), 5.97 (d, 2H, H_{JJ} = 3.75, ph ring), 5.72 (d, 2H, H_{JJ} = 3.75, ph ring), 2.90 (sep, 1H, Ar_(p-cy)), 2.51 (s, 3H, CH₃), 2.01 (s, 3H, CH₃Ar_(p-cy)), 1.34 (d, 6H, H_{JJ} = 4.00, CH₃Ar_(p-cy)), 1.22 (d, 6H, H_{JJ} = 4.25, CH₃Ar_(p-cy)); ¹³C NMR (400 MHz, CD₃CN): δ = 160.26, 153.42, 138.21, 135.71, 132.90, 132.02, 130.65, 129.47, 128.82, 102.73, 90.82, 85.34, 82.51, 31.26, 21.12, 16.54; ESI-MS: 613.93 [M⁺] peak, 578.98 [M⁺-Cl] peak, 236.08 [(p-cy)RuCl⁺] peak; UV-Vis {CH₃CN, λ_{max} nm (ε, M⁻¹ cm⁻¹)}: 227(5800), 330(400); Anal. Calc. for C₂₇H₂₈NSeRuClPF₆ (757.94) (%): C, 42.79; H, 3.72; N, 1.85. Found (%): C, 42.98; H, 3.86; N, 1.96.

2.3.7. [Cp^{*}Rh(Se=PPh₂Py)Cl]PF₆ (7). Color: Red orange precipitate; Yield: 61 mg (81%); IR (KBr, cm⁻¹): 3436(b), 2926(w), 1636(m), 1439(m), 1400(m), 1385(w), 1163(m), 1131(m), 1096(s), 1024(m), 998(w), 861(s), 841(vs), 781(w), 756(m), 716(w), 697(m), 556(vs), 513(s); ¹H NMR (400 MHz, CD₃CN): δ = 9.09 (d, 1H, H_{JJ} = 3.25, py ring), 8.10 (t, 1H, py ring), 7.70 (d, 2H, H_{JJ} = 2.00, ph ring), 7.86-7.74 (m, 5H, ph ring), 7.60-7.52 (m, 4H, ph ring), 7.37 (t, 1H, py ring), 1.42 (s, 15H, Cp^{*} ring); ¹³C NMR (400 MHz, CD₃CN): δ = 158.24, 154.63, 138.95, 134.69, 132.98, 132.25, 130.93, 129.54, 127.02, 97.89, 7.65; ESI-MS: 568.02 [M⁺] peak, 536.01 [M⁺-Se] peak, 236.09 [Cp^{*}RhCl⁺] peak; UV-Vis {CH₃CN, λ_{max} nm (ε, M⁻¹ cm⁻¹)}: 249(4500), 414(400); Anal. Calc. for C₂₇H₃₀NSeRhClPF₆ (761.79) (%): C, 42.57; H, 3.97; N, 1.84. Found (%): C, 42.76; H, 4.08; N, 1.93.

2.3.8. [Cp^{*}Ir(Se=PPh₂Py)Cl]PF₆ (8). Color: Yellow precipitate; Yield: 67 mg (65%); IR (KBr, cm⁻¹): 3436(b), 2924(w), 1624(w), 1455(m), 1439(m), 1384(m), 1133(w), 1099(s), 1033(m), 998(w), 862(s), 841(vs), 782(m), 755(m), 731(w), 715(w), 691(m), 556(s), 512(s); ¹H NMR (400 MHz, CD₃CN): δ = 9.03 (d, 1H, H_{JJ} = 3.25, py ring), 8.15 (t, 1H, py ring), 7.88 (d, 2H, H_{JJ} = 2.50, ph ring), 7.79-7.60 (m, 5H, ph ring), 7.59-7.55 (m, 4H, ph ring), 7.43 (t, 1H, py ring), 1.43 (s, 15H, Cp^{*} ring); ¹³C NMR (400 MHz, CD₃CN): δ = 158.24, 153.92, 138.86, 135.23, 132.76, 132.89, 131.64, 129.72, 126.61, 97.72, 8.29; ESI-MS: 706.04 [M⁺] peak, 626.08 [M⁺-Se] peak, 363.07 [Cp^{*}IrCl⁺] peak; UV-Vis {CH₃CN, λ_{max} nm (ε, M⁻¹ cm⁻¹)}: 226(7600), 307(1300), 386(400); Anal. Calc. for C₂₇H₃₀NSeIrClPF₆ (851.10) (%): C, 38.10; H, 3.55; N, 1.65. Found (%): C, 38.26; H, 3.62; N, 1.78.

2.4. Syntheses of metal complexes (9)-(12)

$[(\text{arene})\text{RuCl}_2]_2$ or $[\text{Cp}^*\text{MCl}_2]_2$ (0.1 mmol), $\text{Ph}_2\text{PyP}=\text{O}$ (0.2 mmol) and NH_4PF_6 (2 molar equivalent) were stirred for 4 h in methanol. The yellow solution was evaporated under reduced pressure. The yellow residue was dissolved in dichloromethane and filtered. The filtrate was concentrated to 2 ml and an excess of hexane was added for precipitation. The yellow product was washed with diethylether and dried under vacuum. Spectroscopic data of **9-12** were in agreement with the previously reported complexes [19].

3. Results and discussion

3.1. Synthesis of the complexes

The chalcogenide ligands $\text{E}=\text{PPh}_2\text{Py}$ {E = S (**L2**); Se (**L3**)} are prepared by direct oxidation using S/Se powder of 2-pyridyldiphenylphosphine (**L1**) in toluene. After evaporation of solvent, crystalline solids are being formed directly from the reaction mixture. The reaction of $[(\text{arene})\text{RuCl}_2]_2$ {arene = benzene; *p*-cymene} and $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir) with 2 molar equivalents of $\text{E}=\text{PPh}_2\text{Py}$ (E = S, Se) afford mononuclear cationic complexes, $[(\text{arene})\text{Ru}(\kappa^2-(\text{NE})-\text{PPh}_2\text{Py})\text{Cl}]^+$ and $[\text{Cp}^*\text{M}(\kappa^2-(\text{NE})-\text{PPh}_2\text{Py})\text{Cl}]^+$, in methanol (scheme 1). These complexes are isolated in very good yield by using PF_6^- as counter ion and purified by recrystallization. All these complexes are obtained as yellow-orange crystalline non-hygroscopic, air-stable solids. They are highly soluble in acetone, acetonitrile and DMSO but are sparingly soluble in methanol, dichloromethane and chloroform. All these complexes are fully characterized by IR, ^1H NMR, mass and electronic spectroscopy.

Preparation of $\text{O}=\text{PPh}_2\text{Py}$ (**L4**) is done by addition of excess aqueous H_2O_2 (30%) to a THF solution of the PPh_2Py as per the reported procedure [4, 6]. We expected formation of $[(\text{arene})\text{Ru}(\kappa^2-(\text{NO})-\text{PPh}_2\text{Py})\text{Cl}]^+$ and $[\text{Cp}^*\text{M}(\kappa^2-(\text{NO})-\text{PPh}_2\text{Py})\text{Cl}]^+$ complexes when reacted with $[(\text{arene})\text{RuCl}_2]_2$ {M = Ru, arene = benzene; *p*-cymene} and $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir). Instead $[(\text{arene})\text{Ru}(\kappa^2-(\text{PN})-\text{PPh}_2\text{Py})\text{Cl}]^+$ and $[\text{Cp}^*\text{M}(\kappa^2-(\text{PN})-\text{PPh}_2\text{Py})\text{Cl}]^+$ have been isolated as an unexpected product and formation of complexes is unambiguous. It could be deoxygenation of $\text{Ph}_2\text{PyP}=\text{O}$ with emphasis on the reductive cleavage of $\text{P}=\text{O}$ bonds, while the relatively weaker $\text{P}=\text{S}$ and $\text{P}=\text{Se}$ bonds are stable under similar reaction environment. Our group has already reported a series of arene Ru and $\text{Cp}^*\text{Rh}/\text{Cp}^*\text{Ir}$ complexes containing PPh_2Py by direct reaction. The dinuclear complexes $[(\text{arene})\text{RuCl}_2]_2$ {M = Ru, arene = benzene; *p*-cymene} and $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir) undergo bridge cleavage reaction with PPh_2Py yielding cationic P,N-chelating complexes. All these complexes are well studied by spectroscopic techniques [11-13], but the crystal structures of **9** and **12** are not published before; so we present them here to establish the structure and composition of the molecules.

3.2. IR studies of the complexes

IR spectra of the mononuclear complexes exhibit strong bands around 1580 and 1455 cm^{-1} , corresponding to the stretching frequencies of $\text{C}=\text{C}$ and $\text{C}=\text{N}$ of phenyl and pyridine rings of the chalcogenide ligand, respectively. $\text{P}=\text{E}$ bond stretching frequencies of the metal complexes show a strong band at 625 and 520 cm^{-1} for $\text{P}=\text{S}$, $\text{P}=\text{Se}$, respectively, in the lower frequency region when free ligand shows these bands at 645 and 567 cm^{-1} [20]. Besides these signals, all the complexes have sharp bands at 841 and 558 cm^{-1} , which correspond to $\text{P}-\text{F}$ stretching frequency of the counter ion [21].

3.3. NMR studies of the complexes

^1H NMR spectra of all metal complexes exhibit three resonances for protons of the pyridyl ring at 9.38, 7.70 and 7.10 ppm, whereas diphenyl protons exhibit two multiplets at 7.80 to 7.70 and 7.60 to 7.50 ppm, similar to the pattern of free ligand except these signals are shifted downfield [22]. Complexes **1** and **5** display a singlet at 6.35 ppm for protons of the arene ligand. Complexes **2** and **6** show two doublets at 6.30 and 6.02 ppm which correspond to the aromatic *p*-cymene ring CH protons, septet at 3.04 ppm as well as a doublet at 1.35 ppm for protons of the isopropyl group and a singlet at 2.04 ppm for methyl proton of *p*-cymene. The Cp^*Rh complexes (**3** and **7**) and Cp^*Ir complexes (**4** and **8**) display a singlet at 1.75 and 1.76 ppm due to the Cp^* ligand, which is slightly downfield in comparison to the starting materials. Due to ligand coordinated, the signals are shifted to downfield compared to free ligand, which indicates the formation of mononuclear complexes [23].

^{13}C -NMR spectra also show signals expected for metal coordinated arene/ Cp^* groups and the $\text{E}=\text{PPh}_2\text{Py}$ ligand. All complexes exhibit nine clusters of peaks from 160.10 to 126.25 ppm for pyridyl and phenyl ring carbons of ligand. The arene ruthenium complexes (**1** and **5**) display a peak at 120 ppm and **2** and **6** display seven peaks from 100-115 ppm, which is typical for arene ligand. Complexes **3**, **4**, **7** and **8** show a sharp singlet at 8.50 ppm that correspond to Cp^* methyl carbon, signals are shifted downfield compared to the metal precursor and free ligand which indicates formation of metal complexes [24].

3.4. Mass studies of the complexes

Mass spectral analyses have been recorded in CH_3CN and m/z values are listed in the Experimental section. The mass spectra of all complexes display prominent peaks corresponding to the molecular ion fragment, in agreement with the theoretically expected values. In ESI spectra, parent peaks have been found (m/z) from thio metal complexes at 509.90 (**1**), 566.10 (**2**), 568.00 (**3**), 658.90 (**4**) and seleno metal complexes at 557.89 (**5**), 613.93 (**6**), 615.90 (**7**) and 706.04 (**8**). These signals show loss of chloride ions from molecular ion peak. All the complexes show $[(\text{arene}/\text{Cp}^*)\text{MCl}^+]$ ion fragment, which indicates stronger bond between the metal ion and arene ligand [25].

3.5. Molecular structural studies

The molecular structures of the complexes have been determined by single crystal X-ray analysis. ORTEP diagrams of the complexes are shown in figures 1-3. Crystallographic and structure refinement parameters are given in table 1. Selected bond lengths and angles are presented in table 2. Complexes **2**, **6**, **7** and **8** show a typical three-legged piano stool structure with the metal center coordinated by chloride and the chelating ligand in $k^2\text{-N,S/Se}$ mode as the legs and the $\eta^6\text{-arene/Cp}^*$ ligand occupying three facial coordination (figures 1 and 2). The metal has pseudo-octahedral arrangement and with formation of a five-membered metallacycle. Hexafluorophosphate is the counter ion in all the complexes. The complexes have normal bond distances and angles but slightly vary in bond distances and bond angles between sulfur and selenium ligand to the metal. The average metal to carbon and centroid of the arene/ Cp^* ring distances in all complexes are 2.158(4) to 2.196(4) Å and 1.677 to 1.796 Å. The metal to chloride and metal to nitrogen bond distances are 2.3815(12) to 2.4034(17) Å and 2.123(3) to 2.109(5) Å, respectively, which are almost identical to earlier reported values [26-28].

The metal to sulfur bond length of **2** is 2.3729(14) Å, that is close to reported values [(arene)Ru(NS)Cl]⁺ {where NS is (2-arylthio-methyl)pyridine 2.3771(18) to 2.374(9) Å [29]; N-[2-(arylthio)-ethyl]morpholine 2.3742(14) to 2.3815(12) Å [30]; 1-pyrimidyl-3-methyl-imidazolyl-2-thione 2.3933(9) Å [31]}. The metal to selenium bond lengths of complexes are 2.5185(5) Å (**6**), 2.5201(5) Å (**7**) and 2.5189(7) Å (**8**), longer than [(arene/Cp*)M(NSe)Cl]⁺ {where NSe is (2-arylseleno-methyl)pyridine 2.4879(7) Å [29]; N-[2-(arylseleno)ethyl]-morpholine 2.4837(14) Å [30]} and smaller than {6-selenopurine and 6-selenoguanine 2.5337(8) to 2.5574(9) Å [32]} and [(arene/Cp*)M(Se∩Se)Cl]⁺ {where Se∩Se is 1,2-bis(phenylseleno)ethane 2.4579(13) to 2.4864(12) Å [33]; bis(diphenylphosphino)amino-dichalcogenide 2.5266(8) to 2.5361(11) Å [34]} in which such a bond length is close to reported values. In all the complexes, the P=S/Se bond distances are longer than that of the free ligand but the C-N bond distances of the complexes are slightly elongated on coordination. The bite angle N-M-S/Se and bond angles N-M-Cl and S/Se-M-Cl are close to 90°. These bond distances and various bond angles support piano stool geometry about the metal center and are in agreement with the values reported in the literature of other closely related complexes [25, 35, 36]. In all the complexes, a number of interesting weak interactions like C-H...Cl and $\pi\cdots\pi$ interactions have been observed in the solid state packing which play a vital role in the building of supramolecular motifs and dominant role in stabilizing the stacking of molecules [37-39]. For example, **7** assembles the inverted piano stool dimeric complex formed by weak interaction of C-H... π contact between the Cp* CHs and diphenyl ligand with distance 3.329 Å (figure 4a).

Complexes **9** and **12** are expected to have a three-legged pseudo octahedral piano stool structure with the chelating derivative ligand in k^2 -PN mode in a four-membered metallacycle (figure 3). X-ray crystallography of these complexes show no significant difference in bond distances and lengths, related to previous reported half sandwich arene Ru complexes with 2-pyridyldiphenylphosphine [12, 13, 16]. Complex **12** crystallizes with one water in a centrosymmetric supramolecular dimer. Two water molecules bridge two molecules of metal bound chloride and pyridyl ring pair related *via* weak interaction of O-H...Cl, O...C-H/O...H-C contacts with bond distances 2.673 Å, 3.195 Å and 2.465 Å, giving a R₄⁴(12) metallorganic dimeric unit (figure 4b) [40].

3.6. UV-Vis studies of the complexes

UV-visible spectra of the complexes were recorded in acetonitrile $\sim 10^{-4}$ M concentration solution from 200-550 nm. All the complexes show intense absorption at 226-335 nm, assigned to $\pi\text{-}\pi^*/n\text{-}\pi^*$ transition. Low intensity band at 375-420 nm corresponds to metal ligand charge transfer transition (MLCT), from excitation of electrons from the metal t_{2g} level to the π^* orbitals of the ligands [41].

4. Conclusion

Cationic arene Ru and Cp*Rh/Cp*Ir complexes containing chalcogenide derivative ligands E=PPh₂Py (E=S, Se) have been synthesized and characterized. X-ray crystallographic analysis confirmed that the complexes have three-legged piano stool geometries. Solid-state structure of complexes show weak interactions like O-H...Cl, C-H... π and $\pi\cdots\pi$ short contacts which play an essential role in stabilizing the stacking of molecules.

Supplementary material

CCDC-1050876 (2), 1050877 (6), 1050878 (7), 1050879 (8), 1050874 (9) and 1050875 (12) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing 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.

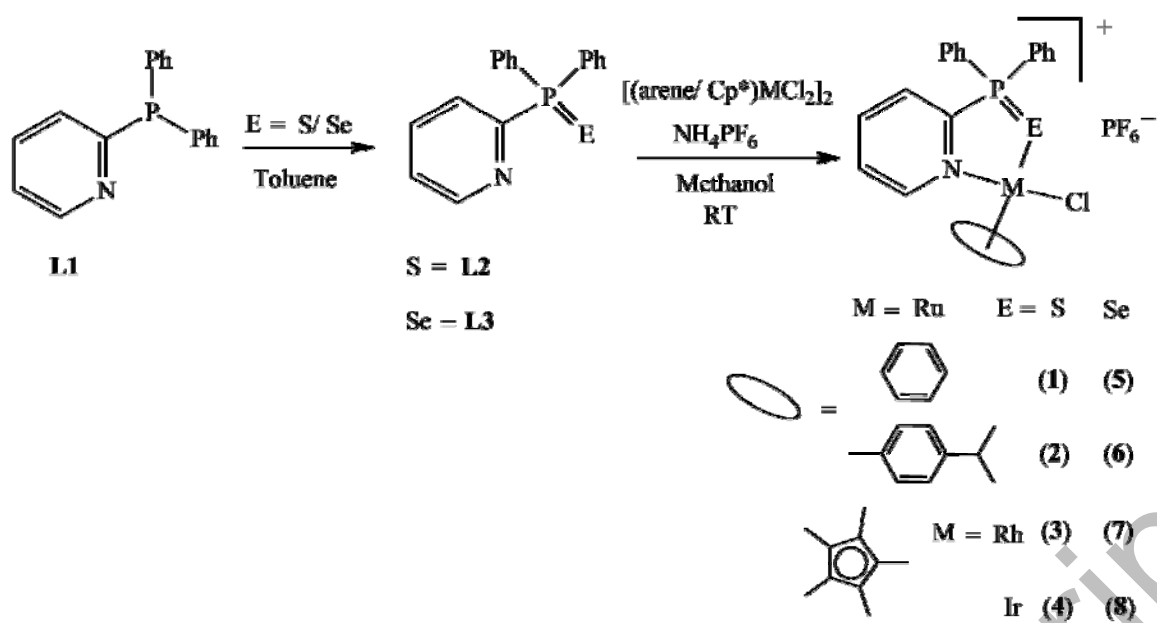
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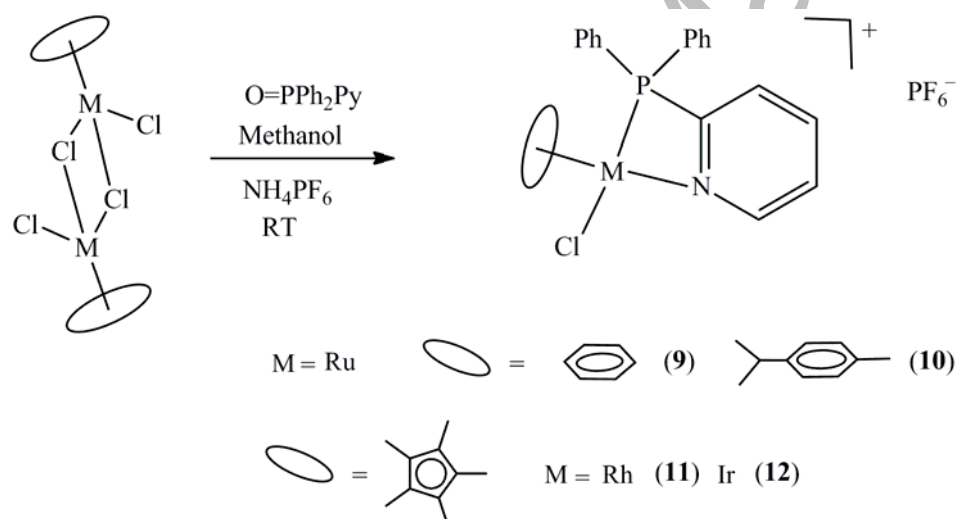
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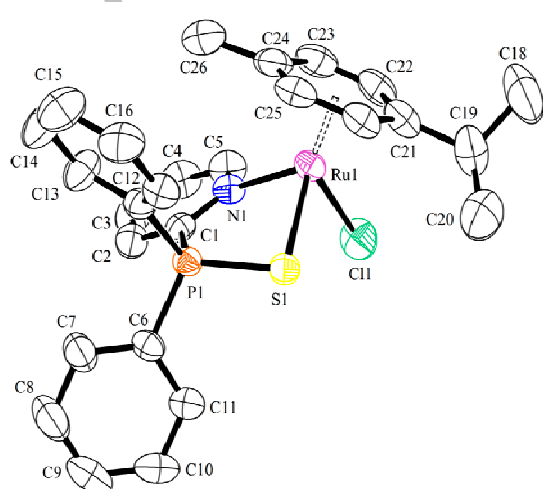
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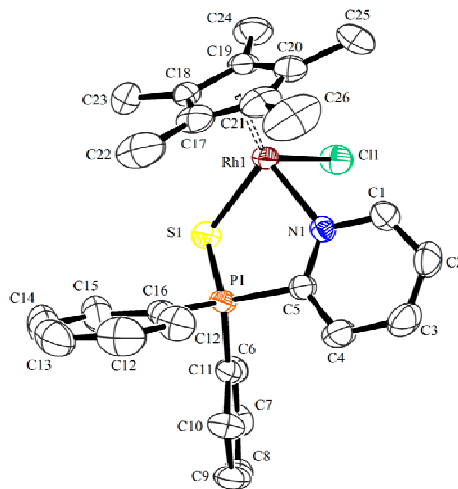
Scheme 1. Preparation of metal complexes with E=PPh₂Py.



Scheme 2. Preparation of metal complexes with O=PPh₂Py.



Complex (2)



Complex (3)

Figure 1. Molecular structures of $[(p\text{-cymene})\text{Ru}(\text{S}=\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**2**) and $[\text{Cp}^*\text{Rh}(\text{S}=\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**3**) with 50% probability thermal ellipsoids. Counter ion and hydrogens are omitted for clarity.

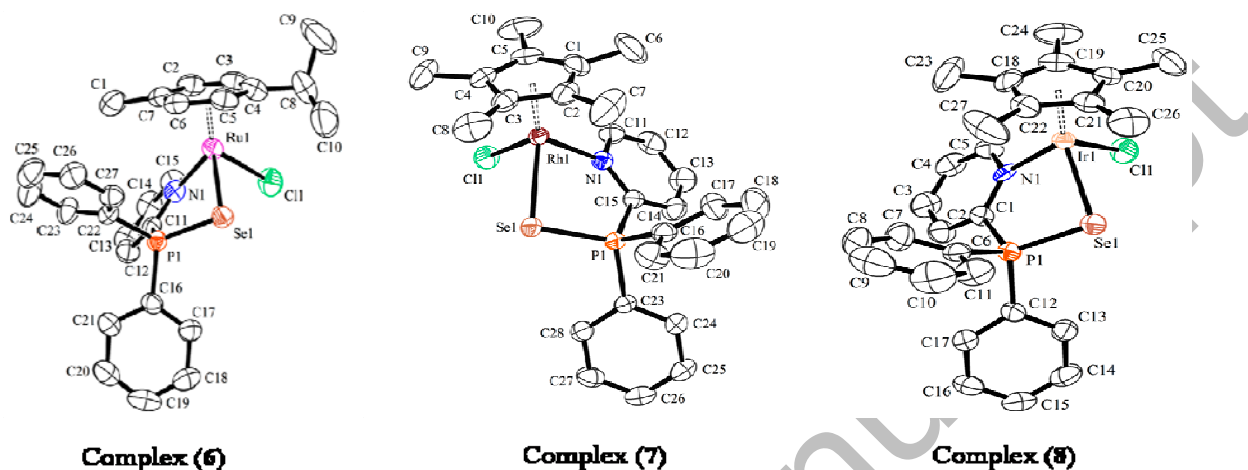


Figure 2. Molecular structures of $[(p\text{-cymene})\text{Ru}(\text{Se}=\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**6**), $[\text{Cp}^*\text{Rh}(\text{Se}=\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**7**) and $[\text{Cp}^*\text{Ir}(\text{S}=\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**8**) with 50% probability thermal ellipsoids. Counter ion and hydrogens are omitted for clarity.

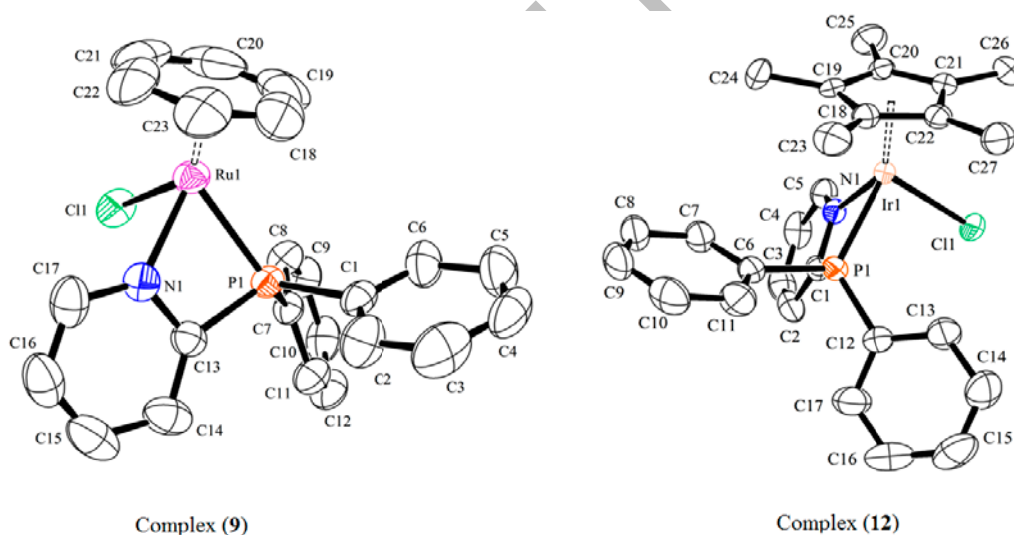


Figure 3. Molecular structures of $[(\text{benzene})\text{Ru}(\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**9**) and $[\text{Cp}^*\text{Ir}(\text{PPh}_2\text{Py})\text{Cl}]\text{PF}_6$ (**12**) with 50% probability thermal ellipsoids. Counter ion, hydrogens and solvent molecule are omitted for clarity.

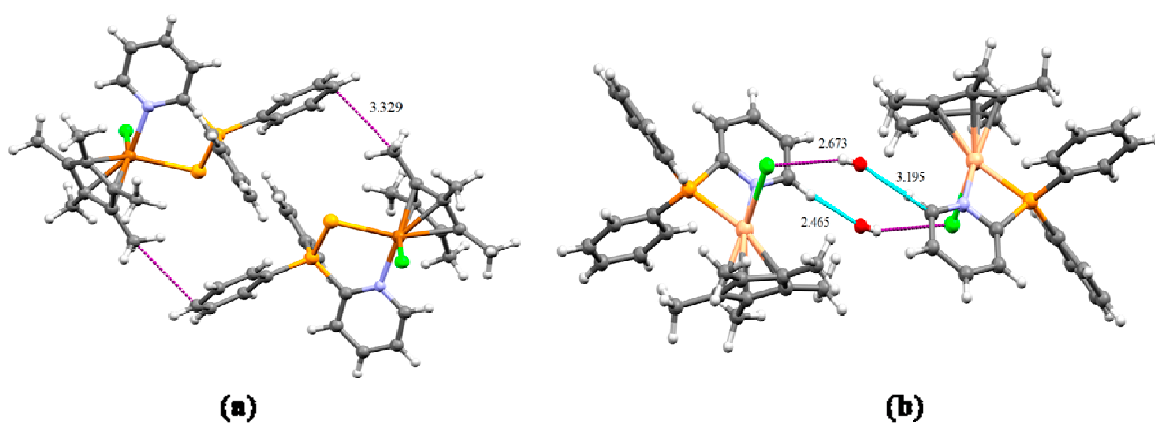


Figure 4. (a) View of **7** showing the dimeric pair of π -- π interaction; (b) View of **12** showing the dimeric pair of O-H--Cl interaction and C-H--O interaction along with water molecule.

Table 1. Crystallographic and structure refinement parameters for complexes.

	2	6	7	8	9	12. H ₂ O
Empirical formula	C ₂₇ H ₂₈ ClF ₆ NP ₂ Ru	C ₂₇ H ₂₈ ClF ₆ NP ₂ RuS	C ₂₇ H ₂₉ ClF ₆ NP ₂ RhS	C ₂₇ H ₂₉ ClF ₆ IrNP ₂ S	C ₂₃ H ₂₀ ClF ₆ NP ₂ R	C ₂₇ H ₂₉ ClF ₆ IrNOP
Formula weight	S	e	e	e	u	2
Temperature (K)	711.02	757.92	760.77	850.06	622.86	789.12
Wavelength (Å)	292.5(3)	291.77(12)	293(2)	293(2)	291.59(18)	290.6(2)
Crystal system, space group	Monoclinic, <i>P21/n</i>	Monoclinic, <i>P21/n</i>	Triclinic, <i>P</i> $\overline{1}$	Triclinic, <i>P</i> $\overline{1}$	Monoclinic, <i>P21/n</i>	Monoclinic, <i>P21/c</i>
Unit cell dimensions	a = 11.1428(2) Å α = 90° b = 15.3394(3) Å β = 92.528(17)° c = 17.4201(3) Å π = 90°	a = 11.2530(3) Å α = 90° b = 15.3439(6) Å β = 93.267(3)° c = 17.3956(5) Å π = 90°	a = 8.6448(4) Å α = 98.170(5)° b = 11.3839(9) Å β = 97.718(4)° c = 15.5573(7) Å π = 100.918(5)°	a = 8.7145(4) Å α = 98.245(3)° b = 11.3780(5) Å β = 97.406(3)° c = 15.6374(5) Å π = 100.845(3)°	a = 11.1146(4) Å α = 90° b = 15.8780(4) Å β = 91.261(3)° c = 13.8150(3) Å π = 90°	a = 11.9797(3) Å α = 90° b = 7.9851(16) Å β = 96.924(2)° c = 30.6201(6) Å π = 90°
Volume (Å ³)	2974.63(10)	2998.74(17)	1467.43(15)	1487.56(10)	2437.46(12)	2907.73(12)
Z, Calculated density (Mg/m ³)	4, 1.588	4, 1.679	2, 1.722	2, 1.898	4, 1.701	4, 1.798
Absorption coefficient (mm ⁻¹)	0.851	1.988	2.079	5.965	1.000	4.855
F(000)	1432	1512	756	820	1240	1536
Crystal size (mm)	0.25 × 0.22 × 0.13	0.15 × 0.12 × 0.08	0.25 × 0.21 × 0.18	0.28 × 0.28 × 0.28	0.21 × 0.21 × 0.12	0.29 × 0.25 × 0.19
Theta range for data collection	3.455 to 28.352°	3.625 to 27.83°	3.969 to 28.462°	3.711 to 28.216°	3.422 to 28.336°	3.934 to 28.407°
Limiting indices	-13 ≤ h ≤ 12, -19 ≤ k ≤ 19, -22 ≤ l ≤ 21	-14 ≤ h ≤ 14, -20 ≤ k ≤ 11, -22 ≤ l ≤ 11	-10 ≤ h ≤ 11, -15 ≤ k ≤ 13, -20 ≤ l ≤ 20	-10 ≤ h ≤ 11, -13 ≤ k ≤ 15, -20 ≤ l ≤ 18	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -8 ≤ l ≤ 18	-11 ≤ h ≤ 14, -9 ≤ k ≤ 9, -36 ≤ l ≤ 24
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Reflections collected / unique	13287 / 5185 [R(int) = 0.0272]	13347 / 5131 [R(int) = 0.0287]	12213 / 5691 [R(int) = 0.0212]	12202 / 5711 [R(int) = 0.0389]	11100 / 4657 [R(int) = 0.0207]	12297 / 4790 [R(int) = 0.0231]
Completeness to theta = 25.242	99.8 %	99.8 %	99.7 %	99.8 %	99.7 %	99.8 %
Data / restraints / parameters	6799 / 0 / 352	6784 / 0 / 349	6722 / 0 / 352	6722 / 0 / 345	5533 / 0 / 308	5112 / 0 / 357
Goodness-of-fit on F ²	1.019	1.027	1.043	1.052	1.102	1.299
Final R indices [I > 2σ(I)]	R1 = 0.0456, wR2 = 0.1094	R1 = 0.0451, wR2 = 0.1054	R1 = 0.0382, wR2 = 0.0982	R1 = 0.0427, wR2 = 0.1016	R1 = 0.0654, wR2 = 0.1720	R1 = 0.0392, wR2 = 0.0705
R indices (all data)	R1 = 0.0659, wR2 = 0.1223	R1 = 0.0677, wR2 = 0.1183	R1 = 0.0487, wR2 = 0.1057	R1 = 0.0550, wR2 = 0.1085	R1 = 0.0767, wR2 = 0.1820	R1 = 0.0431, wR2 = 0.0716

Largest diff. peak and hole (e.A ⁻³)	0.736 and -0.582	0.953 and -0.860	1.085 and -0.725	1.667 and -1.365	3.841 and -0.831	1.688 and -1.145
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Table 2. Selected bond lengths (Å) and angles (°) of **2**, **6-9** and **12**.

Complex	2	6	7	8	9	12
M(1)-P(1)	-	-	-	-	2.3208(12)	2.3113(13)
M(1)-E(1)	2.4094(9)	2.5185(5)	2.5201(5)	2.5189(7)	-	-
M(1)-N(1)	2.123(3)	2.127(3)	2.125(3)	2.109(5)	2.118(4)	2.150(5)
M(1)-Cl(1)	2.3815(12)	2.3867(13)	2.3924(9)	2.4034(17)	2.3860(13)	2.3944(14)
P(1)-E(1)	1.9819(13)	2.1384(11)	2.1329(9)	2.1463(16)	-	-
M(1)-C _{ave}	2.191(4)	2.196(4)	2.158(4)	2.166(7)	2.193(7)	2.184(5)
M(1)-CNT	1.677	1.683	1.788	1.796	1.699	1.810
N(1)-M(1)- P(1)/E(1)	86.25(9)	86.87(9)	87.30(7)	87.98(13)	66.97(12)	66.89(12)
P(1)/E(1)-M(1)-Cl(1)	85.27(4)	85.25(4)	89.81(3)	87.32(5)	88.54(4)	89.65(5)
N(1)-M(1)-Cl(1)	82.70(9)	83.40(10)	85.45(8)	83.95(14)	82.37(12)	82.45(12)

CNT represents the centroid of the arene/Cp* ring; C_{ave} represents the average bond distance centroid of the arene/Cp* ring carbon and metal atom.

Graphical abstract

