Abstract

The reaction of Pd(OC(O)CF$_3$)$_2$ and Pd(OC(O)Bu)$_2$ carried out separately with LH$_2$$_{2,5}$-tolyl in 1:1 ratio in toluene at 70 °C for 6 h afforded six-membered $[C,N]$ palladacycles [Pd{$\kappa^2$(C,N)-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}{$\mu$-OC(O)R}]$_2$ (Ar = 4-MeC$_6$H$_4$, R = CF$_3$ (I);‘Bu (II)) in 91 and 92 % yields, respectively. Palladacycle I was subjected to a metathetical reaction with LiBr in aq. ethanol at 80 °C for 3 h to afford bromo bridged six-membered $[C,N]$ palladacycle [Pd{$\kappa^2$(C,N)-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}{$\mu$-Br}]$_2$ (Ar = 4-MeC$_6$H$_4$) (III) in 95% yield. Palladacycles I and III were subjected to a bridge splitting reaction with Lewis bases (L’s) in CH$_2$Cl$_2$ separately at ambient temperature to afford monomeric six-membered $[C,N]$ palladacycles [Pd{$\kappa^2$(C,N)-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}(OC(O)CF$_3$)(L)] (Ar = 4-MeC$_6$H$_4$; L = 2,6-Me$_2$C$_5$H$_3$N (IV), 1,3,5-triaza-7-phosphaadamantane (PTA) (V), [Pd{$\kappa^2$(C,N)-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}Br(L)](Ar= 4-MeC$_6$H$_4$; L = 2,6-Me$_2$C$_5$H$_3$N (VI), PTA (VII)) in 93–96% yield. Further, palladacycle III was treated with Na(acac) (acac: acetylacetonate) in CH$_2$Cl$_2$ at ambient temperature to afford aspirocyclic six-membered $[C,N]$ palladacycle [Pd{$\kappa^2$(C,N)-C$_6$H$_3$Me-5(NHC(NHAr)(=NAr))-2}{$\kappa^2$-O,O’-acac)}(Ar= 4-MeC$_6$H$_4$; VIII) in 93% yield. The molecular structures of I–VI were determined by single crystal X-ray diffraction data. Palladacycles I and II exist as a dimer in transoid in-in conformation in the solid-state. Palladacycle III was shown to possess a transoid arrangement with two halves of the molecule related by a centre of symmetry and the [Pd($\mu$-Br)$_2$Pd]$^{2+}$ unit was shown to be planar. Palladacycles IV–VI are monomeric with the Lewis base placed trans to the imine nitrogen around the palladium atom due to antisymbiosis.

Cyclometalation resistant sym N,N’,N”-tris(2,5-xylyl)guanidine, ArN=C(NHAr)$_2$ (Ar = 2,5-Me$_2$C$_6$H$_3$; LH$_2$$_{2,5}$-xylyl) was designed, isolated in 85% yield and characterized by microanalytical, IR, mass spectral data, NMR ($^1$H, and $^{13}$C) data, and single crystal X-ray diffraction data. LH$_2$$_{2,5}$-xylyl was shown to possess anti-anti αβ conformation in the solid state. The reaction of trans-[Cl$_2$Pd(PhCN)$_2$] and Pd(OC(O)R)$_2$ with two equiv of LH$_2$$_{2,5}$-xylyl carried out separately in toluene under reflux condition for 12 h afforded trans-[X$_2$Pd(ArN=C(NHAr)$_2$)$_2$] (Ar = 2,5-Me$_2$C$_6$H$_3$; X = Cl (IX), OC(O)R; R = Me (X), Ph (XI), and ‘Bu (XII)), and palladium(IV) oxo guanidine complex, [(CF$_3$C(O)O)$_2$Pd(O)(ArN=C(NHAr)$_2$)$_2$] (XIII)
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in > 90% yield. Adducts IX–XII and palladium(IV) oxo guanidine complex, XIII were characterized by microanalytical, IR, NMR (1H, and 13C) data and single crystal X-ray diffraction data. The stereochemical information around the square planar palladium, the disposition of the C=N double bond of the one guanidine with respect to the C=N double bond of the other guanidine, orientation of the xylyl moiety of the –NHAr units with respect to the C=N unit of the guanidine, and orientation of o-Me substituent of the xylyl substituent with respect of plane of the CN3 unit were analyzed and turn out to be trans syn anti-anti ααβ/βαβ (IX), trans anti anti-syn βαβ/ααβ (X), trans anti-syn ββα/ααβ (XI), and trans anti-anti ββα/ααβ (XII). The palladium atom in the adduct XIII revealed a square pyramidal geometry with two basal positions occupied by the oxygen atom of the monodentate trifluoroacetate moiety in trans disposition as was the imine nitrogen atom of the guanidine unit and the apical position was occupied by the oxo ligand. In solution, adducts IX and XII were shown to exist as a single isomer whereas X and XI were shown to exist as a mixture of two isomers in about 1:1 ratio as revealed by room temperature 1H and 13C NMR data and a variable temperature 1H NMR data and NOESY NMR data measured at 243 K in the case of XI. Adducts X and XI in solution were shown to exist as a mixture of trans anti anti-syn and trans anti anti-anti isomers and were shown to interconvert via the restricted C–N(H)Ar bond rotation. Adducts IX–XIII were shown to be effective precatalysts for Heck coupling reaction involving chlorobenzene and methylacrylate.

The reaction of cis-[Cl2Pt(S(O)Me2)2] with one equiv of sym N,N′,N″ triarylguanidines, ArN=C(NHAr)2 (Ar = 2-MeC6H4 (LH22-tolyl), 2-(MeO)C6H4 (LH22-anisyl), 4-MeC6H4 (LH22-tolyl), 2,5-Me2C6H3 (LH22,5-xylyl), and 2,6-Me2C6H3 (LH22,6-xylyl)) carried out separately in toluene under reflux condition for 3 h afforded 1:1 adducts [Cl2Pt(S(O)Me2)(ArN=C(NHAr)2)] (ArN=C(NHAr)2: LH22-tolyl (XIV), LH22-anisyl (XV), LH22-tolyl (XVI), LH22,5-xylyl (XVII), and LH22,6-xylyl (XVIII)) in 83–99% yield. The reaction of cis-[Cl2Pt(S(O)Me2)2] with one equiv of LH22-anisyl in the presence of one equivalent of NaOAc in methanol under reflux condition for 3 h afforded six-membered [C,N] platinacycle, [Pd{κ2(C,N)-C6H3(OMe)-3(NHC(NHar)(=NAr)=2)Cl(S(O)Me2)} (Ar = 2-(MeO)C6H4; XX) in 93% yield and the same reaction carried out with bulkier LH22-tolyl and LH22,5-xylyl for 12 h afforded
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six-membered \([C,N]\) platinacycles, \([\text{Pd}\{\kappa^2(C,N)-\text{C}_6\text{H}_3\text{Me}_y\text{-}z(\text{NHC}(\text{NHAr})(=\text{NAr})-\text{2})\text{Cl}(\text{S(O)Me}_2)\}]\) \((x = 3, y = 1, z = 3; \text{Ar} = 2\text{-MeC}_6\text{H}_4\text{ (XXI)}; x = 2, y = 2, z = 3,6; \text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3\text{ (XXII)})\) in 92 and 89\% yield, respectively. The reaction of cis-\([\text{Cl}_2\text{Pt}(\text{S(O)Me}_2)_2]\) with one equiv of \(\text{LH}_2^{2\text{-tolyl}}\) and \(\text{LH}_2^{4\text{-tolyl}}\) carried out separately in the presence of one equivalent of NaOAc in methanol under reflux condition for 3 h afforded acetate substitution products, \(\text{trans}-(\text{AcO})\text{ClPt}(\text{S(O)Me})(\text{L})\) \((\text{L} = \text{LH}_2^{2\text{-tolyl}}\text{ (XXIII)}, \text{L} = \text{LH}_2^{4\text{-tolyl}}\text{ (XXIV)})\) in 93\% yield. The new compounds were characterized by IR, NMR \(\text{(^1H, ^13C, and ^195Pt)}\), micro-analytical and mass spectral data. The platinum atom in adducts XIV, XVII, and XVIII was shown to exhibit a \text{trans} configuration whereas that in XV and XXIII was shown to exhibit a \text{cis} configuration. The sulfur atom of \(\text{Me}_2\text{S(O)}\) was shown to coordinate to the platinum atom in XX in \text{cis} relation with respect to the aryl carbon. Compound XXIII represents the first structurally characterized acetate substitution product in the cyclometalation reaction mediated by external base, NaOAc. Factors responsible for the observance of cyclometalation products (XX–XXII) versus substitution products (XXIII and XXIV) and the overall mechanism of C–H activation process were discussed in light of the conformations, and steric/electronic properties of the guanidines.