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Chlorometallate and palladium cluster complexes of wide-span diimine and diamine ligands

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Abstract

Diimine and diamine ligands that are unable to coordinate to a single metal favour the formation of unusual, high-nuclearity Zn chlorometallate and palladium chloride complexes.

Introduction

Ligands that can promote the assembly of multiple metal cations into precisely-structured arrangements are highly desirable as these multimetallic motifs impact on a diverse range of chemical topics such as catalysis,\textsuperscript{1} bio-inorganic chemistry,\textsuperscript{2} medicine,\textsuperscript{3} and single molecule magnetism.\textsuperscript{4} In particular, ligand designs incorporating 1,4-disubstituted arenes have been intensively investigated as platforms that favour bi- and multinuclear complex formation due to the inability of the two donors to chelate to a single metal cation.\textsuperscript{5} For example, imine and amine acyclic ligands,\textsuperscript{6} marocycles,\textsuperscript{7} and cryptands\textsuperscript{8} derived from 1,4-disubstituted arenes have been developed and show a propensity to form polynuclear complexes, although in simple systems cyclometallation reactions at the central aryl ring are observed, particularly with late transition metals.\textsuperscript{9}

We are interested in developing straightforwardly-synthesised and inexpensive ligands for the assembly of multinuclear complexes of metals from across the Periodic Table,\textsuperscript{10} in particular to access new chemistry that can occur within well-defined cavities such as found in Pacman complexes,\textsuperscript{11} and related supramolecular assemblies.\textsuperscript{12} We report here on the use of new wide-span diimine and diamine ligands as outer and inner-sphere coordination platforms for the generation of new, high-nuclearity chlorometallate and palladium chloride complexes. The use of durene in the ligand design ensures that undesired cyclometallation reactions are minimised.

\textbf{Scheme 1.} Synthesis of wide-span diimine (L\textsubscript{Im}) and diamine (L\textsubscript{Am}) ligands and their chlorometallate and cluster complexes. Reagents and conditions: (i) H\textsubscript{2}NR/Ar, MeCN; (ii) H\textsubscript{2}NR/Ar, MeCN; (iii) NaBH\textsubscript{4}, MeOH, R = \textsuperscript{t}Bu; (iv) 2 HCl, Et\textsubscript{2}O, CoCl\textsubscript{2}; (v) 2 HCl, Et\textsubscript{2}O, 4 ZnCl\textsubscript{2}; (vi) 3 PdCl\textsubscript{2}(MeCN)\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}.
The pro-ligands L\textsuperscript{Im} and L\textsuperscript{Am} were synthesised in high yield from the readily available precursors 1 and 2 through straightforward bromide substitution and Schiff-base condensation routes, respectively (Scheme 1). Borohydride reduction of diimine L\textsuperscript{ImR} proved to be the most reproducible route to diamine L\textsuperscript{AmR}. The 2,6-diisoproparyl-substituted diimine L\textsuperscript{ImAr} and diamine L\textsuperscript{AmAr} compounds were crystallised from saturated solutions of MeCN and their X-ray crystal structures determined (Fig. 1). In the solid state, both L\textsuperscript{ImAr} and L\textsuperscript{AmAr} form extended structures through intermolecular hydrogen-bonding interactions and display no solvent incorporation. In L\textsuperscript{ImAr} (Fig. 1, top), the imine N1-C13 bonds (1.236(2) Å) adopt an anti-conformation (torsion angle = 180.0(2)°) and are offset by 29.8(3)° with respect to the central aryl ring. The sterically-demanding \textsuperscript{3}Pr substituents on the terminal aryl groups result in an approximately orthogonal orientation (72.7(2)°) of this aryl ring to the imine N=C group. This orientation results in an intermolecular interaction between the C10 isopropyl methyl hydrogens and the central aryl ring (C10⋯C16 = 3.745(4) Å), so forming a chain motif in the extended structure. Reduction of the N=C double bond in L\textsuperscript{ImAr} to form L\textsuperscript{AmAr} allows free rotation around the N1-C13 single bond (1.489(2) Å) and results in a different structure in the solid state (Fig. 1, bottom) in which the N1-C13 bonds adopt a syn-conformation (torsion angles = 79.9(2)/84.0(2)°). As with L\textsuperscript{ImAr}, the steric demand of the \textsuperscript{3}Pr\textsubscript{2}(C\textsubscript{6}H\textsubscript{3}) substituent results in an approximately orthogonal orientation of this group in relation to the amine N1-C13 bond (76.1(2)/68.2(2)°), but in this case the presence of the amino hydrogen results in a hydrogen bond between the two amines (N1⋯N1’ = 3.264(2) Å); \pi-H interactions are also seen in the extended structure.

The coordination chemistry of these ligands was investigated (Scheme 1). Reactions between L\textsuperscript{Im} or L\textsuperscript{Am} and either CoCl\textsubscript{2} or ZnCl\textsubscript{2} in THF showed little change in the resonances for L in the \textsuperscript{1}H NMR spectra. However, the use of CDCl\textsubscript{3} as the NMR solvent resulted in the crystallisation of the chlorometallate salts [H\textsubscript{2}L\textsuperscript{AmR}][CoCl\textsubscript{4}] and [H\textsubscript{2}L\textsuperscript{ImR}][Zn\textsubscript{4}Cl\textsubscript{10}], presumably as a result of the presence of adventitious HCl in

**Figure 1.** Ball and stick representations of the X-ray crystal structures of diimine L\textsuperscript{ImAr} (left) and diamine L\textsuperscript{AmAr} (right). For clarity, all hydrogen atoms except those involved in hydrogen bonding are omitted.
Scaled-up reactions were carried out in which the ligands were protonated by HCl (2 eq) in Et₂O prior to the addition of CoCl₂ (1 eq) or ZnCl₂ (4 eq) in Et₂O. This latter procedure resulted in the formation of analytically pure materials. The X-ray crystal structures of both [H₂L²₅⁵][CoCl₄] and [H₂L²⁶²][ZnCl₁₀] were determined (Fig. 2) and show that the protonated ligands interact with the chlorometallate salts through a series of hydrogen-bonding interactions; all hydrogens involved in hydrogen-bonding were located in the difference Fourier map and refined with riding thermal parameters and bond distance restraints.

**Figure 2.** Ball and stick representations of the X-ray crystal structures of [H₂L²₅⁵][CoCl₄](H₂O)(CHCl₃) (top) and [H₂L²⁶²][ZnCl₁₀] (bottom). For clarity, CHCl₃ solvent of crystallisation and all hydrogen atoms except those involved in hydrogen bonding are omitted.

In the solid state structure of [H₂L²₅⁵][CoCl₄] (Fig 2., top) the amine appendages adopt a syn-conformation (torsion angle = 6.5(3)°) that results in a hydrogen-bonded cavity suited for chlorometallate recognition (over chloride), with N-H···Cl and C-H···Cl hydrogen-bonding interactions ranging in distance from 3.165(3) to 3.357(3) Å. The chelation of the cobaltate anion by the wide-span ligand causes some strain, as evidenced by the 10° curvature of the central diaminoarene and the inclusion of a molecule of water that interacts both with the protonated amine (N1···O1 2.817(5) Å) and the cobaltate (Cl4···O1 3.165(3) Å); as with the free ligands above, other intra- and intermolecular close contacts (to CHCl₃ solvent of crystallisation) are present in the extended structure.

In the solid state structure of [H₂L²⁶²][ZnCl₁₀] (Fig. 2, bottom), the protonated imine arms adopt an anti-conformation (torsion angle = 176.0(2)°) and the terminal aryl groups, and to a lesser extent the
central arene, are oriented-orthogonally to the N=C bond (torsion angles = 88.1(3) and 53.4(4)°, respectively). As with the cobaltate above, a variety of weak interactions exist between the doubly-protonated diimine and the zincate, with N-H···Cl and C-H···Cl hydrogen bonding interactions ranging in distance from 3.152(3) to 3.759(3) Å. However, in this case, the wide-span ligand framework has favoured the isolation of an unusual Zn₄Cl₁₀²⁻ anionic cluster. In this cluster, each zinc cation is tetrahedral with one terminal chloride and three chlorides bridging to adjacent zinc cations. This results in a rectangular arrangement of zinc cations in which two opposing sides of the rectangle comprise either a single bridging chloride or two bridging chlorides, with Zn···Zn distances of 3.8345(5) Å and 3.1405(5) Å and Zn-Cl-Zn angles of 114.25(3) and 85.30(2)°. Also, the anti-conformation of the imines allows for an intermolecular N1···Cl3 hydrogen bond (3.152(3) Å) from which a linear chain of alternately sandwiched ligand and metallate clusters grows. While Zn₄Cl₁₀²⁻ anionic clusters have been observed before, to our knowledge they adopt adamantane or open-chain structural motifs and not the new rectangular arrangement of Zn cations seen here. Furthermore, metal chloride clusters that adopt a similar structural motif are rare, and limited primarily to α-phenylene-metallated Pt₄ chlorides, Mo₄Cl₁₂³⁻ clusters, and the chlorobismuthate and antimonates M₄Cl₁₈⁶⁻ (M = Bi, Sb). Significantly, the recognition of high-nuclearity chlorometallates by L⁴⁻ and L⁵⁺ may impact on the high-efficiency, hydrometallurgical extraction of base and precious metals.

The reaction between PdCl₂(MeCN)₂ and either L⁴⁻ or L⁵⁺ in CH₂Cl₂ led to the sole formation of the trinuclear palladium chloride cluster [Pd₃Cl₆(L)]; this formulation was supported by elemental analysis. The X-ray crystal structures of [Pd₃Cl₆(L⁴⁻)] and [Pd₃Cl₆(L⁵⁺)] were determined (Fig. 3) and were found to be isostructural; as such, only the former structure will be discussed (Fig.3, top). In a similar manner to [H₂L⁵⁺][CoCl₄], the imine appendages adopt a syn-conformation (torsion angle = 6(2)°) that allows the ligand to chelate to the single Pd₃Cl₆ cluster through the imine nitrogens N1 and N2. Also, the terminal and central aryl rings are similarly tilted with respect to the N=C bond by 67(4) and 73(4)°, respectively. Each Pd cation is square planar but the Pd₁Cl₆ cluster is not linear due to the constraints imposed by the chelating diimine ligand. This feature results in a cradle arrangement in which the Pd₁-Pd₂-Pd₃ angle is 127.4(4)° with Pd(μ-Cl)Pd angles of approximately 90°.

The solid state structure of [Pd₃Cl₆(L⁴⁻)] is retained in solution. In the ¹H NMR spectrum (Fig. S1, Supplementary information), only one imine resonance is seen at 8.38 ppm, whereas two distinct CH₃ environments are seen at 3.75 and 2.09 ppm for the central arene, which reflects the asymmetry of binding to the Pd₃Cl₆ cluster. Furthermore, free rotation about the N-C bond for the terminal 2,6-diisopropyl aryl substituent is hindered, as reflected by the presence of two isopropyl CH resonances at 3.56 and 3.49 ppm and four resonances for the CH₃ environments. The ¹H NMR spectrum of [Pd₃Cl₆(L⁵⁺)] is similar (Fig. S2), indicating that the solid state structure of this complex is also retained in solution, but shows only one resonance for the 'Bu substituent at 1.22 ppm. Furthermore, the ESI mass
spectrum of \([\text{Pd}_3\text{Cl}_6(L^{\text{ImR}})]\) shows an ion at \(m/z\) 682 for the partially-intact cluster \([\text{Pd}_3\text{Cl}_5(L^{\text{ImR}})]^+\), and indicates structural retention in solution.

Figure 3. Ball and stick representations of the X-ray crystal structures of \([\text{Pd}_3\text{Cl}_6(L^{\text{ImAr}})]\) and \([\text{Pd}_3\text{Cl}_6(L^{\text{ImR}})]\). For clarity, disorder components, solvent of crystallisation, and all hydrogen atoms are omitted.

High nuclearity complexes of Pd chloride are rare and the \([\text{Pd}_3\text{Cl}_6(L)]\) complexes can be viewed as short fragments of polymeric \((\text{PdCl}_2)_n\). While postulated through indirect evidence,\(^{18}\) only a single example of the crystallographic characterisation of a \(\text{PdCl}_2\) trimer end-capped by organic ligands has been described;\(^{19}\) in this example, the unusual \(\text{Pd}_3\text{Cl}_6\) motif was stabilised through the use of a large coneangled, bowl-shaped triarylphosphine. Trinuclear PdCl structures are also known for allyl-complexes, although in these cases one chloride has been substituted by the allyl ligand.\(^{20}\) The related dianion \(\text{Pd}_3\text{Cl}_8^{2-}\) has also been characterised structurally as its \(\text{Bu}_4\text{N}\) ammonium salt.\(^{21}\) In all of these previous structures, the \(\text{Pd}_3\text{Cl}_6\) motif is linear, in contrast to the cradle structure seen by us in \([\text{Pd}_3\text{Cl}_6(L)]\). Presumably, this new bent geometry for the \(\text{Pd}_3\text{Cl}_6\) cluster is necessary to allow a good fit to the wide-span diimine ligands. Furthermore, it is evident that methyl substitution of the central arene ligand has ensured that the formation of cyclometallated products is inhibited.
Notes and references


