

Synthesis and Characterization of Gold(I) Complexes of Bis(diphenylphosphino)- acetonitrile

by

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Master of Science

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Declaration 1

Plagiarism

I, Sicelo V. Sithole, declare that the experimental work described in this dissertation was carried out at the School of Chemistry, University of KwaZulu-Natal, Westville campus, between August 2009 and October 2010, under the supervision of Dr. W. E. van Zyl, and that:

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Scientific Contributions

Aspects of this work has already been published and presented.

- S. V. Sithole, R. J. Staples, W. E. van Zyl,
[μ -Bis(diphenylphosphanyl)acetonitrile- κ^2 P:P]bis-[chloridogold(I)],
Acta Cryst. **2011**, E 67, m64. (available online 11 December 2010)
- Sicelo V. Sithole, Richard J. Staples and Werner E. van Zyl, *New Gold(I) Complexes from Deprotonated Acetonitrile: Synthesis and Characterization*. Oral presentation by S.V.S. at the South African Chemical Institute (SACI) Postgraduate Colloquium, University Of KwaZulu-Natal, Pietermaritzburg Campus, 19 May 2010.

Sicelo V. Sithole

Abstract

This study comprised the synthesis and characterization of select phosphine ligands and their complexation to gold(I). An initial approach was the reaction between Ph_2PCl in "wet" organic solvent and $[\text{ClAu}(\text{tht})]$ (tht = tetrahydrothiophene) which led to the complex $[\text{ClAu}\{\text{Ph}_2\text{P}(\text{OH})\}]$, **1**, which was the second polymorph of this complex based on solid state X-ray crystallographic studies. Related to the Ph_2PCl precursor, the study refocused on the preparation of the ligand bis(diphenylphosphino)acetonitrile, $(\text{PPh}_2)_2\text{CHCN}$, ("dppm-CN"), **2**, obtained from a modified literature method. Ligand **2** underwent a facile reaction with either $[\text{ClAu}(\text{tht})]$ or $[(\text{C}_6\text{F}_5)\text{Au}(\text{tht})]$ (molar ratio 1:2) to yield new open-ended dinuclear gold(I) complexes $[(\text{ClAu})_2(\text{dppm-CN})]$, **3**, and $[(\text{C}_6\text{F}_5\text{Au})_2(\text{dppm-CN})]$, **4**, respectively, both in satisfactory yield. Ligand **2** can also be deprotonated to form the anion $[(\text{PPh}_2)_2\text{CCN}]^-$ which reacted with $[\text{AuCl}(\text{tht})]$ (molar ratio 1:1) to form the neutral cyclic dinuclear gold(I) complex $[\text{Au}_2\{(\text{PPh}_2)_2\text{CCN}\}_2]$, **5**. The anion $[(\text{PPh}_2)_2\text{CCN}]^-$ showed unexpected reactivity behaviour toward mono- or bis(phosphine) gold(I) chloride complexes that led to the cleavage and formation of new Au-P bonds. Complexes **1**, **3**, **4**, **5** were all subjected to a single crystal X-ray studies. Complex **1** has a central intermolecular $\text{Au}\cdots\text{Au}$ interaction of 3.0375(2) Å, and peripheral hydrogen bonding ($\text{O-H}\cdots\text{Cl}$) within the structure. Complex **3** displays an intramolecular $\text{Au}\cdots\text{Au}$ interaction of 3.1669(4) Å, but no other intermolecular interactions. The structure of complex **4** reveals a side-by-side "dimer of dimers" structural motif in the solid state and represents a new type of system. Complex **4** contains intramolecular $\text{Au}\cdots\text{Au}$ interactions alternating between 3.0902(7) Å and 3.0809(6) Å, and an intermolecular $\text{Au}\cdots\text{Au}$ interaction of 3.592 Å. The next dimeric unit along the virtual 1D chain is more than 6 Å away. Complex **5** has an intramolecular $\text{Au}\cdots\text{Au}$ separation of 2.8650(4) Å and no intermolecular interactions. The $\text{C}\equiv\text{N}$ bond in **5** is $1.160(7)^\circ$ and is longer relative to the $\text{C}\equiv\text{N}$ bond in complexes **3** and **4**. The new complexes were further investigated by elemental analyses, mass spectrometry, ^1H and ^{31}P solution NMR, and FT-IR. The luminescence properties of the complexes was investigated in the solid state. Results showed **3** to be non- or very weakly emissive at room-temperature, the emission of **4** seems to be quenched by the C_6F_5 group at room temperature and qualitative results for **5** showed luminescence both at room temperature and at 77K.

To My Family

Imagination is the beginning of creation

You imagine what you desire

And you will what you imagine

And at last, you create what you will.

George Bernard Shaw

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Abbreviations and Symbols

mol equiv.	mole equivalents
cm ⁻¹	wavenumbers
°C	degrees Celsius
Å	angstrom
ρ	density
V	volume
GoF on F ²	Goodness of Fit on F ²
μ	Absorption coefficient
dppm	bis(diphenylphosphino)methane
dppe	bis(diphenylphosphino)ethane
dppb	bis(diphenylphosphino)butane
dpph	bis(diphenylphosphino)heptane
dmpm	bis(dimethylphosphino)methane
dmpe	bis(dimethylphosphino)ethane
dppm-CN	bis(diphenylphosphino)acetonitrile
LMCT	Ligand to Metal Charge Transfer
EtOH	ethanol
Et ₂ O	diethyl ether
DCM	dichloromethane (CH ₂ Cl ₂)
THF	tetrahydrofuran
NMR	Nuclear Magnetic Resonance
• ¹ H	Proton Nuclei
• ¹³ C	Carbon-13 Nuclei
• ³¹ P	Phosphorus-31 Nuclei
IR	Infrared
UV	Ultraviolet
ESI-MS	Electron-Spray Ionization Mass Spectrometry
Mp	Melting point

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“It would have been very difficult previously to predict the existence of many of these species (gold compounds); some of them are against all the classical rules of bonding and structure and it is the Au-Au interaction which give them the unexpected stability. So the compounds involved in the chemistry of gold may still hold many surprises, waiting for a synthetic chemist to discover them”

M. Cóncepcion Gimeno and Antonio Laguna

1

Introduction

1.1 Overview

1.1.1 Polymorphism and its Occurrence in Gold Based Complexes

The discovery of polymorphism dates back to 1788 when M.H. Klaproth came to the conclusion that the different forms of calcium carbonate (calcite, vaterite and aragonite) can have the same chemical composition, CaCO_3 .^[1] Polymorphism itself is generally described as the ability of the same chemical substance to exist in at least two different crystalline forms.^[2] The discovery of X-ray diffraction and the establishment of knowledge about atomic groupings,^[3] have led to a major advancement in terms of acquiring in-depth structural understanding about polymorphism. An example is the determination of various forms of 1,3-bis(m-nitrophenyl)urea (MNUP) (Fig. 1.1), in which the β and δ forms are indistinguishable visually, although other techniques such as thermomicroscopy have been used to distinguish them.^[4]

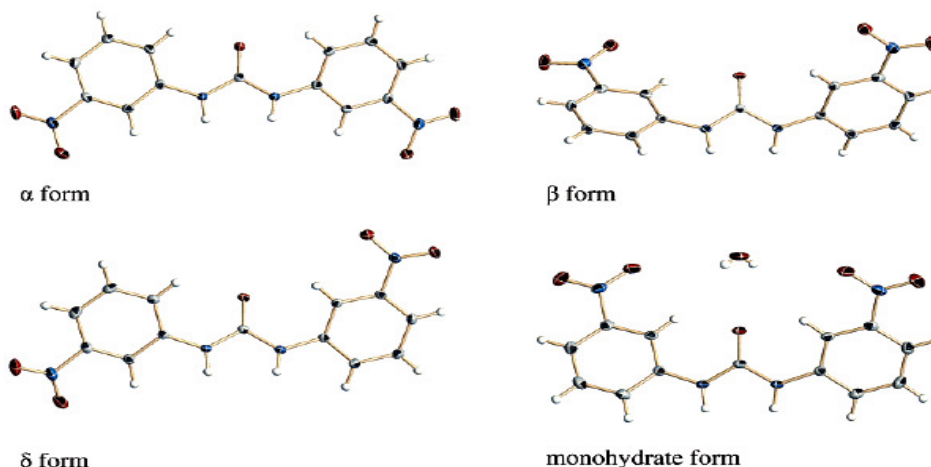


Figure 1.1. Different polymeric forms of 1,3-bis(m-nitrophenyl)urea (MNUP).

With this understanding, information such as molecular conformation, packing arrangements, hydrogen bonding and lattice energies can be deduced and compared in polymorphs.^[5] In addition to different spectroscopic, surface, and chemical properties that polymorphs can possess, the existence of polymorphism in chemical compounds has pronounced effects on the physical properties of the material.^[2] Some of these properties include force-induced emission colour changes or mechanochromic luminescence,^[6] vapochromism^[7] (change of molecular structure through sorption of organic molecule in the vapour phase), magnetic, conducting and zeolitic properties.^[8] The control of a specific polymorphic form is very important, especially in the preparation of pharmaceuticals, explosives, dyes, pigments and flavours.^[4] Control over polymorphism is an important aspect in the field of molecular crystal engineering^[9] where preparation of compounds with well predefined architectures can be made possible.

In gold(I) complexes, polymorphism is of particular interest because of the different luminescent properties that most of these closed-shell d^{10} complexes can possess due to the presence of aurophilic interactions[†] between the neighbouring or adjacent gold(I) centres.^[10] An interesting case on the effect of polymorphism with regards to the optical properties in gold(I) complexes was reported by Balch and co-workers^[11] (Fig. 1.2), in which only one polymorph (hexagonal) of the $[\text{Au}_3(\text{MeN}=\text{COMe})_3]$ complex displayed solvoluminescence.^[12]

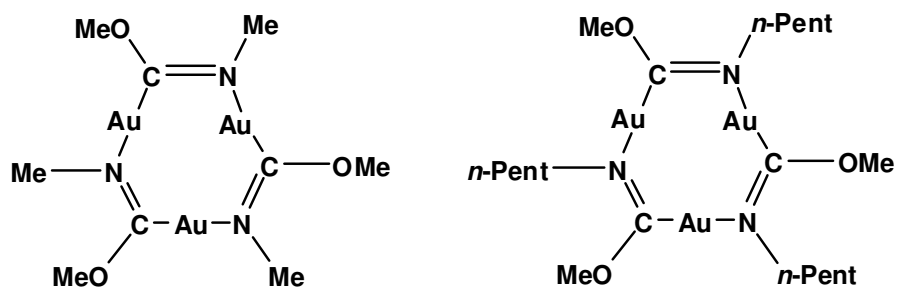


Figure 1.2. Two trinuclear gold(I) complexes that each possess polymorphic forms with different luminescence properties.

[†] See section 1.1.5 for a detailed discussion of aurophilic interactions in gold(I) complexes.

Phosphine-based ligands are amongst the most studied compounds in gold chemistry^[13] and in these systems polymorphism is often observed. Polymorphs of gold based complexes are found associated with simple molecules or in mixed-metal clusters (Fig. 1.3A), where there are metallophilic interactions from other metals such as copper.^[14] The clusters find wide applications as biological lumophores, photonic catalysts and optical materials.^[15] The polymorphs of $[\text{AuCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3\}]$ reported by Fackler and co-workers^[16] depict two distinct packing arrangements in the solid state and different geometric configuration of the cyanide group and this has an influence on the reactivity of the complex towards acids. A more recent study on gold(I) complexes with phosphine ligands having azolyl moieties revealed the formation of seven different polymorphs of the compounds (Fig. 1.3B) with varying intermolecular $\text{Au}\cdots\text{Au}$ interactions, in which these associations tend to stabilise the complexes.^[17]

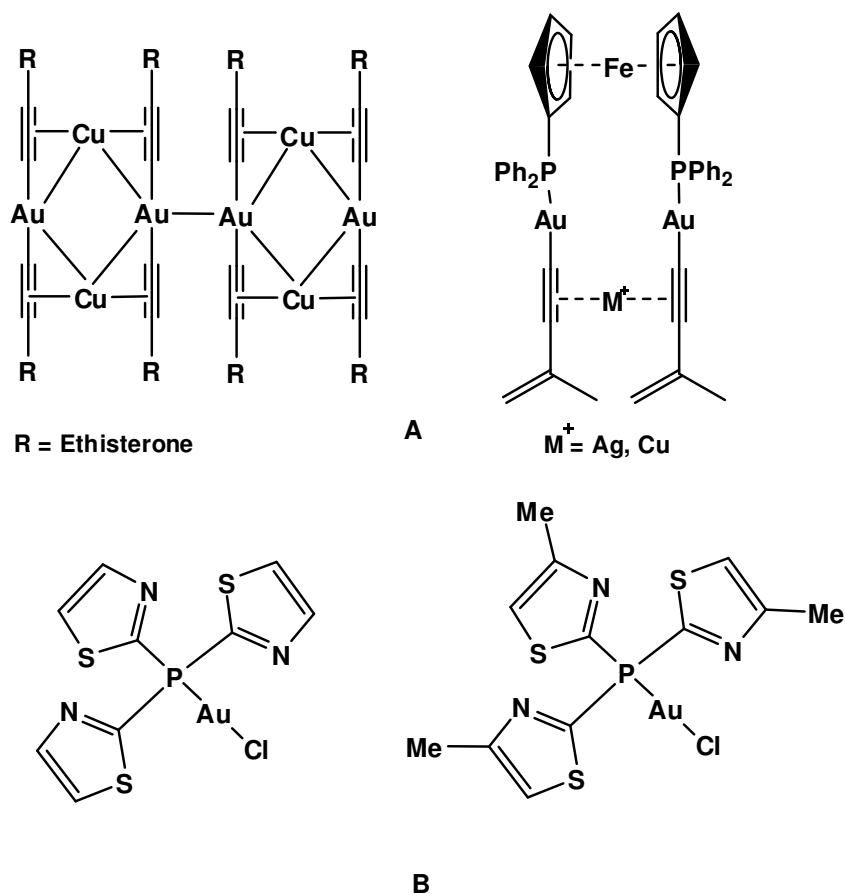


Figure 1.3. (A) Au-M clusters that form polymorphs (B) phosphine based gold(I) complexes with azolyl moieties.^[14, 17]

The use of $[\text{Au}\{\text{PPh}_2\text{C}(\text{CSSC}_6\text{F}_5\text{Au})\text{PPh}_2\text{Me}\}_2][\text{ClO}_4]$ as an optical fiber and volatile organic compound (VOC) sensor,^[8] is evidence of the importance of careful design of the compounds necessary for applications in areas related to environmental issues. The nature and contribution of the aurophilic interactions on polymorphism in gold based polymorphs seem to be significant and bring about interesting variations in optical features. The combination of aurophilic and other molecular properties such as hydrogen bonding, supramolecular organisation and phase changes, is becoming more important in controlling the optical properties of various gold based complexes.^[18] There is no reason to doubt that in future the preparation of 'golden' polymorphs for finding applications as luminescent (LEDs) and vapochromic devices, will be largely based on careful alterations of auro- and metallophilic interactions.^[19]

In this study, a second polymorph of the known complex $[(\text{ClAu})\{\text{Ph}_2\text{P}(\text{OH})\}]$ was obtained serendipitously (see Chapter 2, Section 2.5), and structurally characterized.

1.1.2 Phosphine Ligands: Their Importance in the Coordination Chemistry of Transition Elements

1.1.2.1 Monodentate Phosphine Ligands

Although a pronounced interpretation of chemical reactions involving coordination complexes in essence began with Alfred Werner (1866-1919),^[20] who later received a Nobel Prize (1913) for his insights in providing many solutions to bonding in transition metals,^[21] their existence goes back much earlier. Coordination compounds such as Aureolin ($\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot 6\text{H}_2\text{O}$, yellow) and Prussian blue $\text{K}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]$ have always been used as pigments and date back to historical times.^[20]

Although a vast amount of coordination compounds have been prepared over the years, it should be pointed out that the use of alizarin dye, a calcium chelate compound of hydroxyanthraquinone, was first used in India and was known to the ancient Persians and Egyptians and was reported by Herodotus in *ca.* 450 BC.^[22a] Phosphine-based ligands were not employed before 1857 when A.W. Hoffman reported the first phosphine complexes, those formed through the reactions between triethylphosphine and platinum and gold.^[22b]

A detailed explanation of the bonding between phosphine ligands and transition metals was provided by J. Chatt in the late 1940s.^[22-23] Throughout this period to about the 1960's, major developments of phosphine based complexes have been carried out and the report of Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$, a rhodium(I) complex with a triphenylphosphine unit for catalytic hydrogenation of alkenes in homogeneous solutions, is indication to this advancement.^[24-25]

There has been great progress in the design and synthesis of phosphine-based complexes since this time and many of them have been employed in major chemistry fields such as homogeneous catalysis. Phosphine-based ligands form stable metal complexes with many transition metals in a wide range of oxidation states, the effect is the stabilisation of both low- and high oxidation states through their strong σ -donor and π -acceptor properties.^[24] Another key property of phosphines is the deliberate control over sterics, and this is better understood by a general description termed the cone angle (θ) estimate, first described by Tolman (i.e. Tolman cone angle).^[20] Monodentate phosphines offer much versatility through ease of combination with functional group, the results (Fig. 1.4) are mixed-functional **A**, polydentate **B** and ligands suitable for preparation of water soluble complexes such as 1,3,5-triaza-7-phosphaadamantane (TPA) (**C**) and sulphonated triphenylphosphine $\text{Ph}_2\text{P}(m\text{-HSO}_3\text{C}_6\text{H}_4)$.^[25]

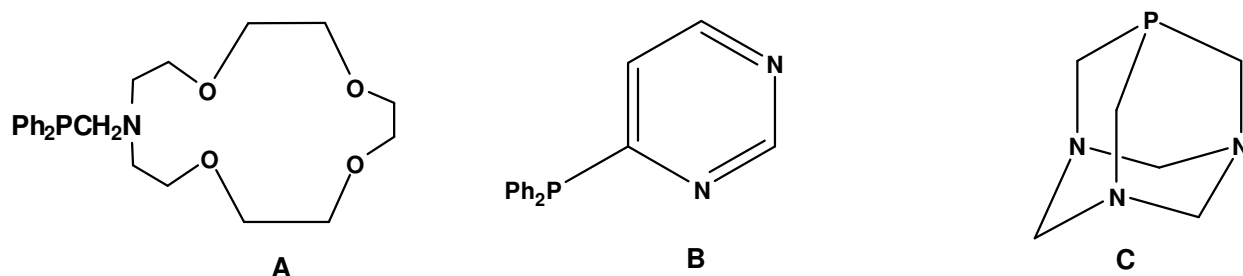


Figure 1.4. Monophosphines with different functionalities for coordination in transition metal chemistry.

The scope of the utility of monodentate phosphine ligands is wide and is not limited only by their use in preparation of metal complexes. Most phosphines serve as nucleophilic catalysts for an array of useful transformations in organic synthesis.^[26] The use of a *P*-chiral phosphine with a ferrocenyl framework for asymmetric catalysis,^[27] and a monomeric tris-

(hydroxypropylphosphine) as a ligand in the preparation of luminescent and stable nanocrystal quantum dots of CdSe/ZnS are a few examples of their adaptability.^[28] In some cases, monodentate phosphines (Fig. 1.5) have been used in conjunction with active metal catalysts for specific reactions, (e.g. palladium catalysed carbon-nitrogen bond forming reactions and TM-catalysed asymmetric reactions)^[29] and thus not necessarily forming metal complexes with transition metals.

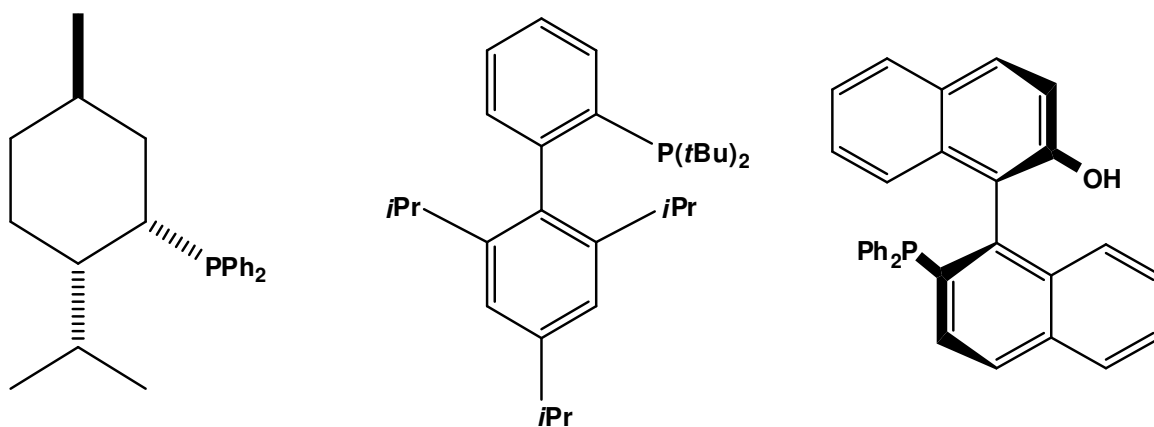


Figure 1.5. Monodentate phosphine ligands used in metal catalysed reactions and asymmetric catalysis.

An extensive study of various metal complexes based on monodentate phosphines has been performed over the years, some examples include complexes of platinum(II),^[30] silver(I),^[31] tungsten(0)^[32] and gold(III)^[33] which find applications in a variety of fields, such as catalysis. Even though monophosphines are essential in the synthesis of numerous interesting compounds as noted above, there is a great deal of work where bidentate bis(phosphine)-type ligands have been employed due to their potential chelating nature and interesting coordination modes to metal centers. From the point of view of experimental gold chemistry with research interests in structure-luminescence relations, the use of bis(phosphines) towards formation of di- or multinuclear gold(I) complexes offers interesting and often very surprising results. This is due to possible formation of unprecedented supramolecular structures due to the nature of the weak intramolecular Au...Au interactions between the gold(I) atoms and possible luminescence properties that can emerge. The use of bis(phosphine) ligands will now be discussed in the

development of several metal complexes, with special attention paid to their contribution towards the development of mono, di- or multinuclear gold complexes.

1.1.2.2 Bidentate Phosphine Ligands: Insights into the Chemistry of bis(diphenylphosphino)-methane (dppm)

The bis(diaryl- and dialkylphosphino)alkanes $[R_2P-(CH_2)_n-PR_2]$ are one of the most important classes and widely used ligands in coordination chemistry^[25], catalysis^[34] and recently in nanochemistry.^[35] The synthesis of bis(phosphines) is generally more complex and time consuming compared to that of monophosphines, and usually involves displacement of halides at $X-(CH_2)_n-X$ with Ph_2P^- nucleophiles, an S_N2 type reaction *via* the use of the readily available reagents such as $LiCH_2PR_2$.^[34] New strategies have been devised and improved syntheses have been reported recently by Slagt *et al.*, on a supramolecular strategy towards preparation of bidentate ligands.^[36] The use of $[R_2P-(CH_2)_n-PR_2]ML_n$ systems is well established and most of these are essential in many catalytic processes.^[37] The ligands dmpe, dppe, dmpm and dppm are amongst the most widely used bis(diaryl- and dialkylphosphino)alkanes and form either bridged (A) or chelated (B) complexes in Fig. 1.6 where only examples of dmpe and dppe are shown.^[25]

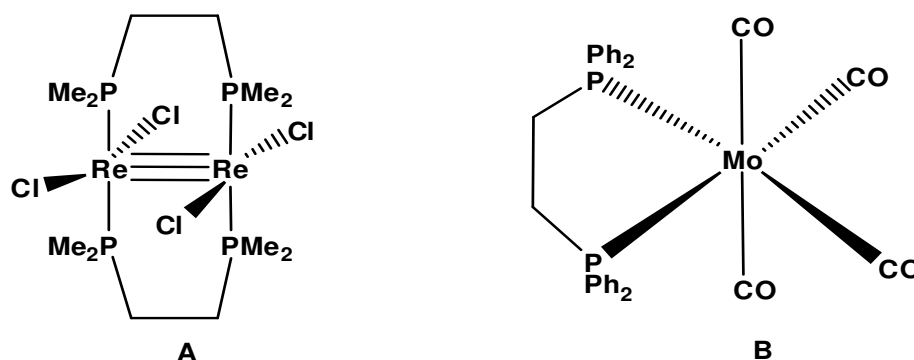


Figure 1.6. Examples of bis(diaryl- and dialkylphosphino)alkanes forming bridging (A) and chelating complexes (B).

The smallest members of the bis(phosphine) ligand family are the bis(dialkyl- and diarylphosphino)*methanes*, $(R_2P-CH_2-PR_2)$ and within the bis(diarylphosphino)alkane family, dppm stands out as one of the best studied systems.^[38] The chemistry of dppm is mostly inspired by its versatility in terms of its coordination modes, i.e. it can act as a chelating or a bridging

ligand as noted previously for most bis(phosphines) (Fig. 1.6). In some instances, dppm has been found to coordinate in a monodentate fashion, with the other PPh₂ group dangling.

Unique to dppm chemistry, Le Floch and co-workers have done interesting work to show that the oxidized sulfur derivative of dppm, [Ph₂P(S)CH₂P(S)Ph₂], can be readily doubly deprotonated to stabilize the dianionic form Li₂[Ph₂P(S)CP(S)Ph₂] very well. By this method, they reported interesting ruthenium^[39a] and uranium^[39b] carbene complexes, to name two examples (Fig. 1.7). It appears work in this area in forming new gold(I) carbene complexes by this route is as yet unexploited.

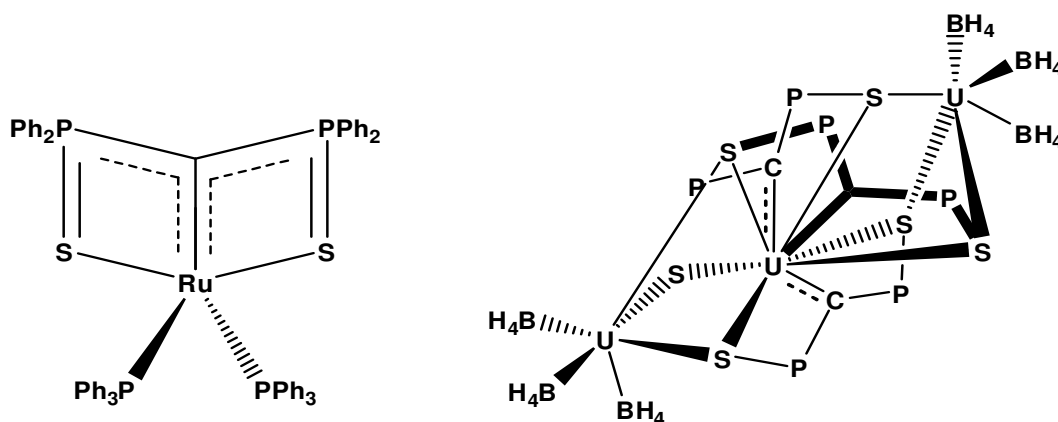


Figure 1.7. Ru(II) and U(IV) carbene complexes from the dianion generated by oxidising dppm with sulfur and treatment with MeLi.

There are numerous examples of dppm-based complexes with dppm coordinating in a chelate fashion, although the chelating effect is not optimum for dppm but for dppe due to the strains associated with the four-membered ring in such complexes.^[38a] Monomeric platinum(II) complexes with dppm in a chelating form have been prepared and compared with the complexes where dppm forms bridged type of systems.^[40] The formation of chelated dppm complexes extends from forming the more abundant systems such as those of Pt(II), or Ir(III), to forming chelated complexes of the less accessible Os(II) species for which the materials are later used in design of phosphorescent OLEDs.^[41] The commercial development of Tc-99m for use in radiopharmaceuticals has also been aided by the role of chelating the dppm ligand to the Tc(II) centre (Fig 1.8).^[42]

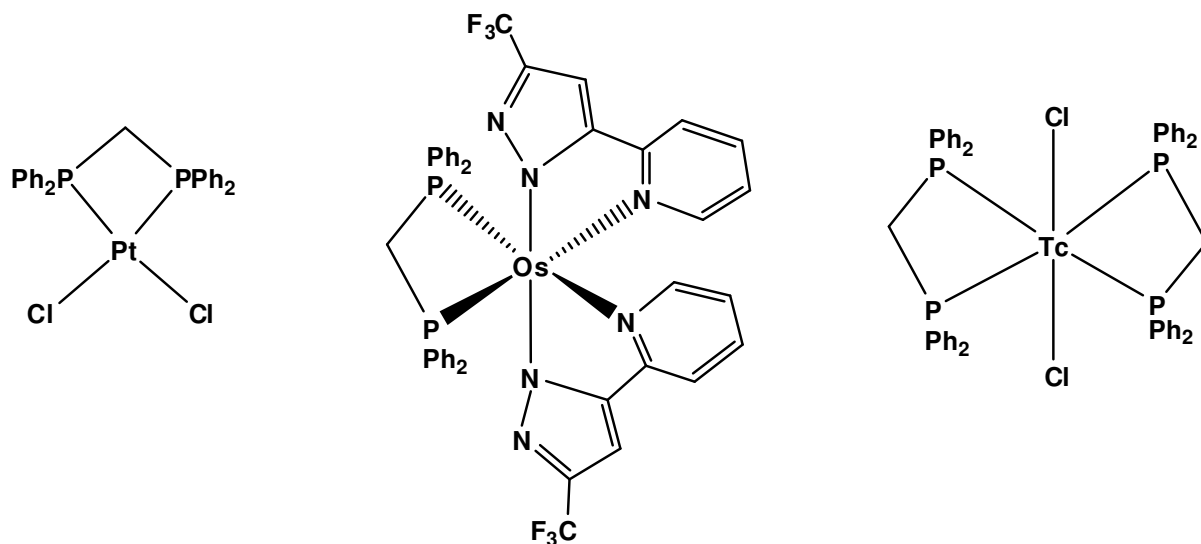


Figure 1.8. The ligand dppm in a chelating coordination mode in Pt(II), Os(II) and Tc(II) complexes.

In gold chemistry complexes with bis(phosphines), (mainly gold(III) complexes) in a chelating fashion are known^[43] although less common compared to gold(I) complexes with bis(phosphines) as a bridging ligand. The ability of bis(phosphines) to form bridged dinuclear metal complexes in general has led to intense exploitation of the chemistry associated with the relationship between two neighbouring centers in understanding their role in catalytic systems,^[38a] especially in gold chemistry where there are areophilic interactions between gold(I) centers which leads to different structural patterns[‡].

Gold complexes with dppm in a bridging coordination mode have been extensively studied over the years and these form neutral open-ended complexes with a general formula $[(X\text{Au})_2(\text{dppm})]$ (X = monodentate anionic ligand) and cationic cyclic structures $[\text{Au}_2(\text{dppm})_2]^{2+}$. The cyclic compounds are not always homobridged, i.e. have dppm ligands on both sides of the metal centers, but may also be heterobridged, i.e. they have a different bridging ligand such as dithiocarbamates, bis(ylide) and dithiophosphinates.^[13a] Gold-based dppm-type complexes have

[‡]Section 1.1.4 outlines the different structural patterns observed in gold(I) bis(phosphine) complexes.

been used as luminescent devices and the cyclic complexes for finding applications as porous materials capable of gas uptake.^[44]

Recently, dppm has been used in the preparation of clusters such as $[\text{Au}_{17}(\text{AsnPr})_6(\text{As}_2\text{nPr}_2)(\text{dppm})_6]\text{Cl}_3$,^[45] $[\text{Ag}_4(\mu\text{-dppm})_2(\mu\text{-C}_2\text{F}_5\text{COO})_4]$,^[46] and $[\text{Rh}_6(\text{CO})_5(\text{dppm})_2(\text{CNR})(\text{C}_{60})_2]$ for use as advanced electronic devices.^[47] In some cases the coordination modes of dppm are used in combination such as those reported by Braunstein *et al.*,^[48] in which there are two dppm units with one in a chelating and the other in a bridging coordination mode in a bimetallic complex.

Whether the role of dppm is that of a chelating or bridging ligand the use of dppm is vast and has always been principally influenced by diverse interests, such as those shown towards preparation of heterobimetallic complexes of platinum and silver for luminescent compounds,^[49] ruthenium-based complexes for models in redox-active metalloproteins,^[50] rare vanadium(IV) complexes^[51] (see Fig. 1.9 for examples) and metal-containing macrocycles and polymers for use in photonics and advanced materials.^[52]

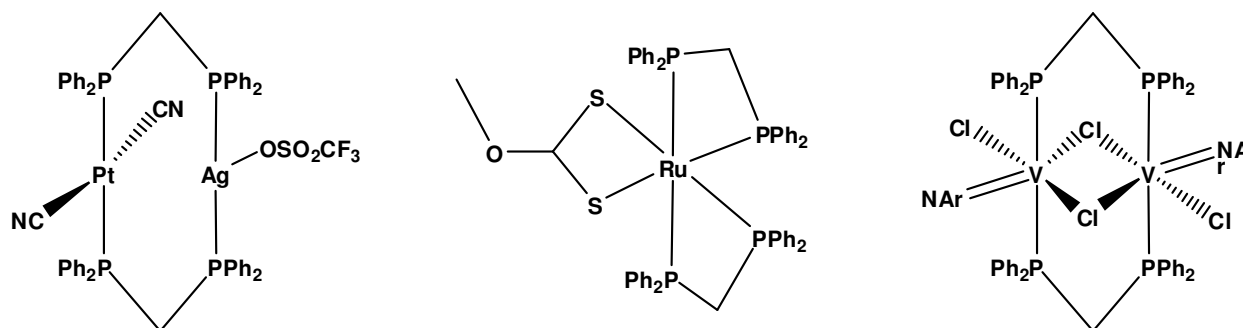


Figure 1.9. The ligand dppm in a chelating and bridging coordinating mode in various TM complexes.

The deprotonation of dppm by strong bases give rise to a bis(phenylphosphino)methanide ligand, $[(\text{PPh}_2)_2\text{CH}]^-$ which offers variation in coordination modes leading to formation of mono-, di- and tetradentate complexes through the phosphorus and carbon donor atoms.^[53, 38a] Chromium complexes of deprotonated and carbon-substituted dppm (with various alkyl units) have been developed for selective oligomerization reactions.^[54] There are a number of gold(I) macrocycles

spectroscopically and structurally characterised that are based on deprotonated dppm,^[38a] and in a study by Usón *et al.*,^[55] their reactivity have been investigated (Fig. 1.10)

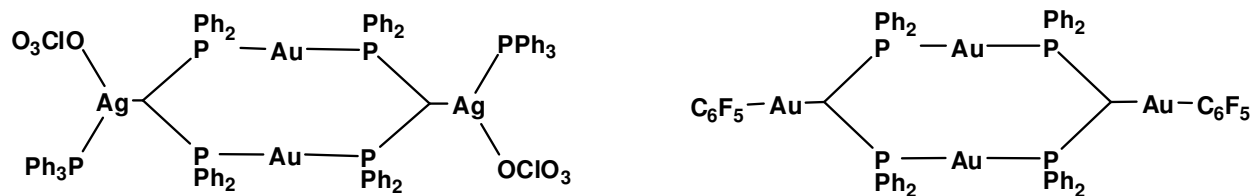


Figure 1.10. The reactivity of cyclic gold(I) complexes towards various Au(I) and Ag(I) compounds.

Derivatives of the $[R_2P-(CH_2)_n-PR_2]$ systems such as the $[R_2P-X-PR_2]$ class ($X = NH$), have also gained considerable attention over the years, with the use of $CH_3(CH_2)_2N(CH_2PPh_2)_2$ in preparation of dendrimer catalysts being one example.^[56]

Ruiz and co-workers have over the years developed the chemistry of the functionalization of $[(PPh_2)_2CH]^-$ with various substituents including the cyano group and thus forming $(Ph_2P)_2CHCN$ or the “dppm-CN” ligand. This was after a study involving cyano activation of $[(PPh_2)_2CH]^-$ as a building block in the synthesis of heterometallic complexes.^[57] Their recent work focuses on functionalizing of manganese complexes with the $[(PPh_2)_2CH]^-$ framework with Se and forming a polyselenide diphosphine^[58] and development of diphosphinoketenimine type ligands, $(PPh_2)_2C=C=NR$.^[59] Chiral heterometalodiphosphines of Ru/Au have been prepared starting with the $[(PPh_2)_2CH]^-$ ligand.^[60] The focus of this dissertation is primarily on the dppm-CN ligand, pathways to preparation and uses in organometallic chemistry will be outlined.

1.1.3 Bis(diphenylphosphino)acetonitrile (dppm-CN)

The bis(diphenylphosphino)acetonitrile, (dppm-CN), ligand has been reported in the literature as the anion $[(PPh_2)_2CCN]^-$ in a phosphorus-organic synthesis^[61] and also as an anionic ligand

(using cyanogen) in a series of heterometallic Ru/Au and Mn/Au complexes (Fig. 1.11).^[57, 53] The reactivity of Mn(I) complexes with the dppm-CN ligand has also been investigated through reactions with halogens (Br₂ and I₂) and pseudohalogens [BrCN, ISePh, (SCN)₂ and (CN)₂].^[62]

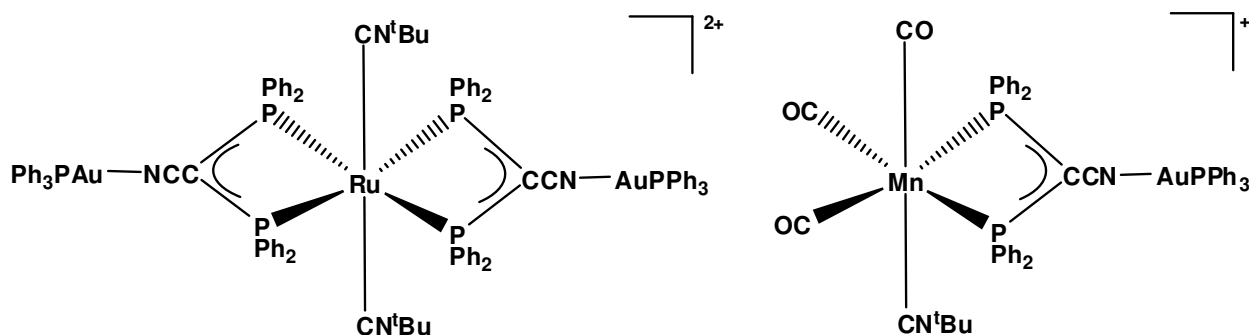
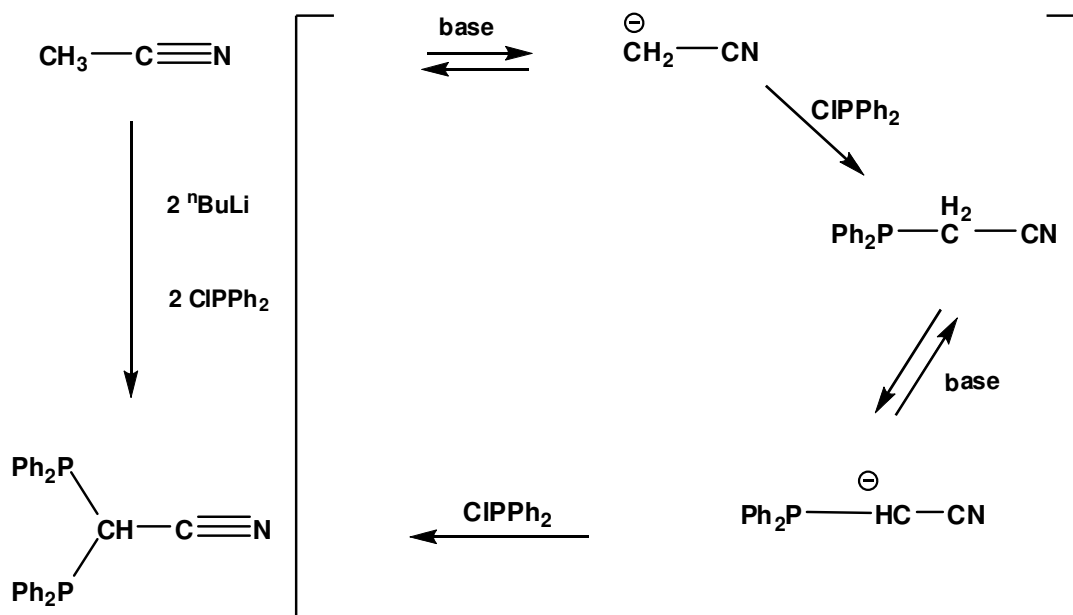


Figure 1.11. The anionic [(PPh₂)₂CCN]⁻ ligand coordinating to heterometallic Ru/Au and Mn/Au complexes.

Until recently the preparation of the dppm-CN ligand involved the use of toxic materials such as (CN), the chemistry of dppm-CN was rejuvenated by Erker and co-workers with facile preparation starting with common acetonitrile^[34,63]. The preparation follows double deprotonation of common acetonitrile with ⁿBuLi to yield the proposed intermediate Li₂[CHCN] (not isolated), which is followed by *in situ* treatment with Ph₂PCl and isolation of the ligand as a minor product from the reaction mixture (Scheme. 1.1).



Scheme 1.1. Formation of dppm-CN from doubly deprotonated acetonitrile.

The observation that the dppm-CN ligand can be isolated from this simple one-pot procedure, has led to studies revealing a number of diverse and fascinating aspects of its chemistry.^[37, 63, 64] This involved derivatising dppm-CN with various reagents (e.g. PhN₃) to form bis(*N*-arylphosphinimino)acetonitrile (which mimics "acac" and "nacnac", two ligands which are frequently used in transition metal chemistry)^[64] and forming complexes of Rh(I) and Ir(I) (Fig. 1.12A and B).

Perhaps the most interesting aspect of newly reported ligand is the sharp increase in acidity by the replacement of a proton with a cyano group on the bridging carbon atom of dppm.^[63] The role of dppm-CN in transition metal chemistry has been demonstrated by reactions of the ligand with various TM [Ru(I), Pd(II) and Pt(II)] with the Pd-based complex (Fig. 1.12 C) reported to be a very active catalyst in the Suzuki-Miyaura coupling reactions.^[37]

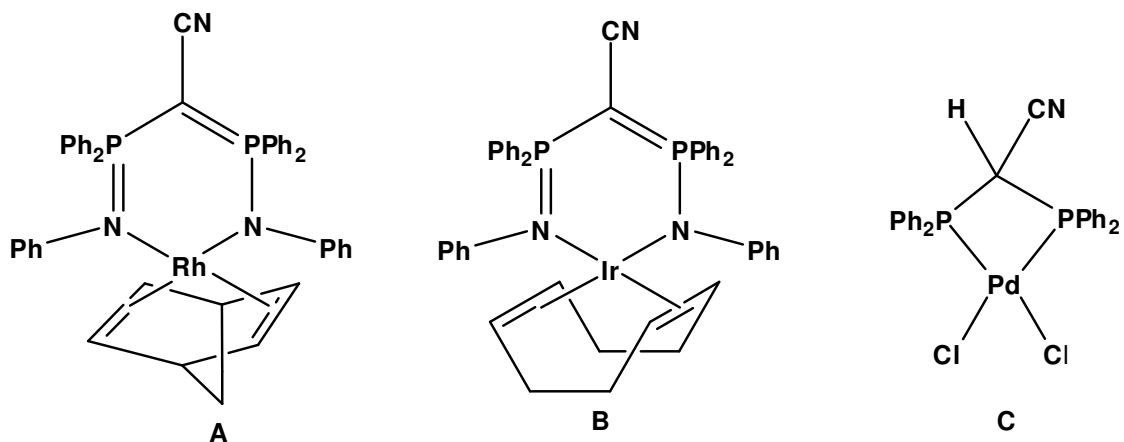


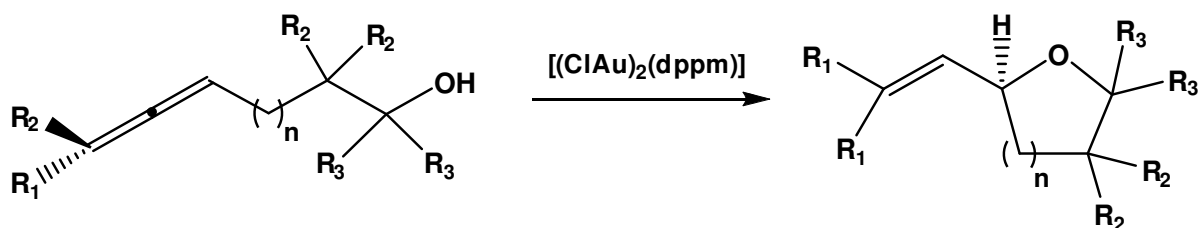
Figure 1.12. Rh and Ir complexes (A and B) from derivatized dppm-CN, and Pd-based dppm-CN complex for Suzuki-Miyaura coupling reactions.

The entry into the chemistry of dppm-CN by a facile synthesis route seemed to open up possibilities in terms of exploitation of the remarkable properties offered by the cyano substituted dppm. The chemistry associated with deprotonated acetonitrile and variation of substituents in the CIPR_2 and stoichiometric ratios in reagents seem to be a fertile one. A range of bis- and tris(phosphine) ligands have been prepared by Erker and co-workers.^[63] This ligand can still be well used in forming complexes with late-transition metals (especially in d^{10} systems), where there is great interest in the synthesis of di- or multimetallic complexes.

Recent work by Nocera and co-workers involved the use of dppm and related ligands in the formation of a series of dinuclear: Au(I)/Au(III), Ir(I)/Ir(III), Ir(0)/Ir(II) and Rh(II)/Au(II) complexes for applications in the development of the chemistry of renewable energy.^[65] The extension of this work has been based on the use of mono- and dinuclear gold(III) complexes in the investigation of halogen photoreductive elimination reactions.^[66] With this brief scope of the use of bis(phosphine) based complexes, it is observed that the role of these systems is crucial in the development of molecular chemistry and the employment of dppm-CN towards the further development of these systems is yet to be explored.

1.1.4 Gold bis(phosphine) complexes

Gold complexes with bis(phosphine) ligands are part of the most used systems in a variety of fields, especially catalysis. The $[(ClAu)_2(dppm)]$ complex has been prepared and used in an intramolecular acetylenic Schmidt reaction, hydroamination of allenes,^[67] and asymmetric hydroalkoxylation reactions (Scheme 1.2).^[68]



Scheme 1.2. Asymmetric hydroalkoxylation catalysis with $[(ClAu)_2(dppm)]$.

Gold complexes with bis(phosphines) with spacers other than the single methylene unit (CH_2) have been studied extensively as well. Koshevoy *et al.*, prepared a series of luminescent dinuclear gold(I) complexes with a bis(phosphines) bridged with 1H-imidazol-1-yl-benzene unit.^[69] A few other examples of gold complexes with bis(phosphines) ligands include open-ended $[(dppm)\{Au(2-SC_6H_4NH_2)\}_2]$ ^[70] and cyclic $[(dppe)\{Au_2(\mu-C_6H_{10})\}]$.^[71] These examples involve the use of thiolates and naphthalenediyl moieties instead of the commonly observed halogens (X_2) in the $[(XAu)_2\{(PPh_2)_2(CH_2)_n\}]$ systems.

Mononuclear gold bis(phosphine) complexes have also been prepared and their luminescence properties investigated.^[72] Contrary to the commonly observed one-dimensional structures observed with gold bis(phosphine) complexes, Lane *et al.*, recently reported three-dimensional self-assembled structures of gold with bis(phosphine) ligands with potential sensor applications or as porous materials for sorption of gases like hydrogen.^[73]

Gold(I) complexes of type $[(XAu)_2\{(PPh_2)_2(CH_2)_n\}]$ ($n = 1-8$) have been prepared and depending on the length of the alkane unit $(CH_2)_n$ between the phosphorus atoms, the complexes form

different structural patterns (Fig. 1.13).^[13] The patterns depicted in **(A)** are mostly associated with complexes with longer alkane units e.g. $n = 4$ or 6 and in this type of systems there are no intra-or intermolecular Au···Au interactions involved. The structural pattern observed in **(B)**, **(C)**, **(D)** and recently in **(E)**^[74] have been observed. The intramolecular Au···Au interactions lead to formation of **(B)**, intermolecular Au···Au interactions in **(D)** in a face-on dimer type, a combination of both intra- and intermolecular Au···Au interactions form 1-D polymeric chains in **(C)** and of discrete dimers **(D)** and **(E)**.^[13]

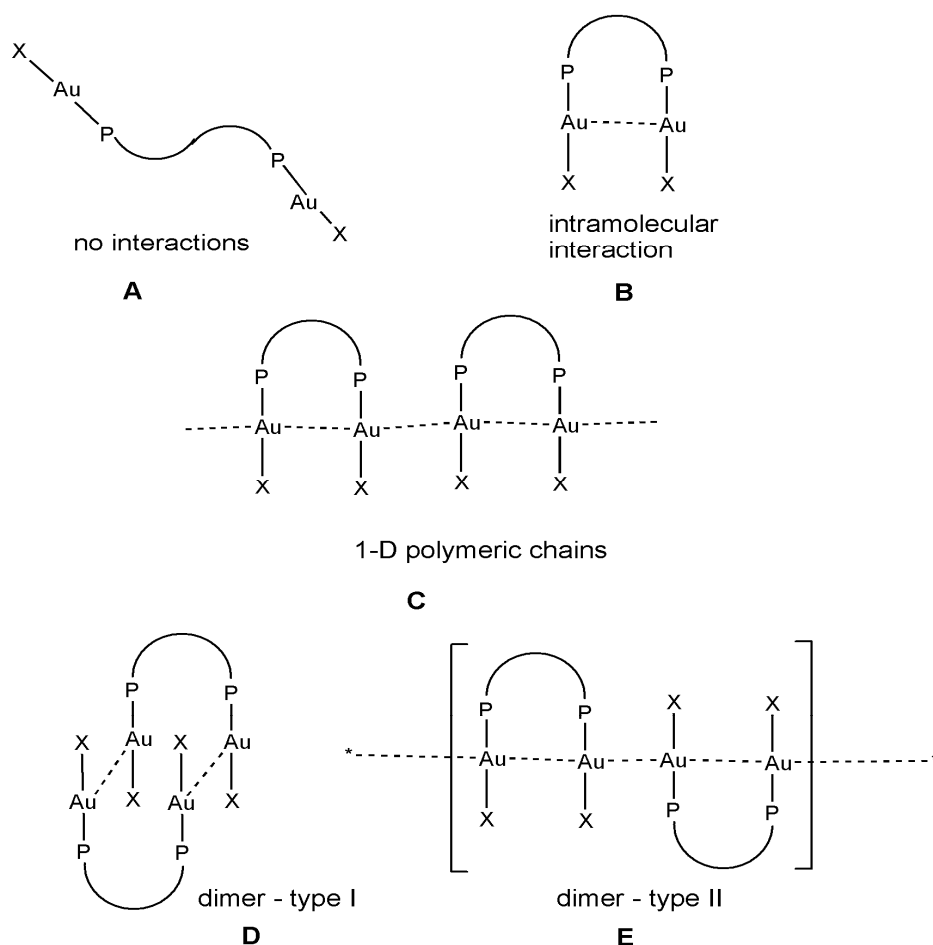


Figure 1.13. Different structural pattern in complexes of type $[(XAu)_2(PPh_2)_2(CH_2)_n]$ (X=halogen).

In a study by Chen and co-workers,^[75] the presence of intramolecular Au···Au interactions in a type **A** system was observed only when there was a switch in patterns from that of **A** to **B** (Fig

1.13) upon treatment with lanthanide(III) compounds. The effect by the differences in the structural patterns is different luminescence properties and polymorphism which have remarkable effects on the properties of gold complexes as highlighted in Section 1.1.1.

1.1.5 Luminescence in Gold(I) Phosphine Complexes

Since the discovery of photoluminescence in phosphine complexes of d^{10} metals in 1970 by Dori and co-workers,^[76] an interest along this field of study was sparked in various research groups and has been ever growing over the years. Although there was not much information at that time regarding the origins of this unique property, an interest in this has been driven by a general observation that amongst the coinage metals, most gold(I) complexes have a tendency to aggregate into oligomers or supramolecular structures through Au...Au interactions with contacts of *ca.* 3.0 Å and possess remarkable photoluminescent properties.^[13, 77]

The weak intra- and intermolecular Au...Au interactions, originally termed "aurophilic interactions" by Schmidbaur,^[78] and their origins are best described by relativistic and correlation effects.^[79] The existence of these weak interactions in many gold(I) complexes have made it possible to study the distinct relationship between the emission energy and the structure of many mono- or dinuclear gold(I) complexes; with observations that the luminescence properties of such complexes can thus be adjusted or fine-tuned through manipulation of the structure.^[80] A study by Yam and co-workers, is a fine example of the manipulation of structure through Au...Au interactions for design of luminescent ion probes for a variety of cations (Fig. 1.14).^[81] It is the combination of both strength (29-46 kJ/mol, i.e. approximating H-bonding)^[82] and directionality^[83] that makes aurophilic interactions particularly attractive for controlling supramolecular structure.

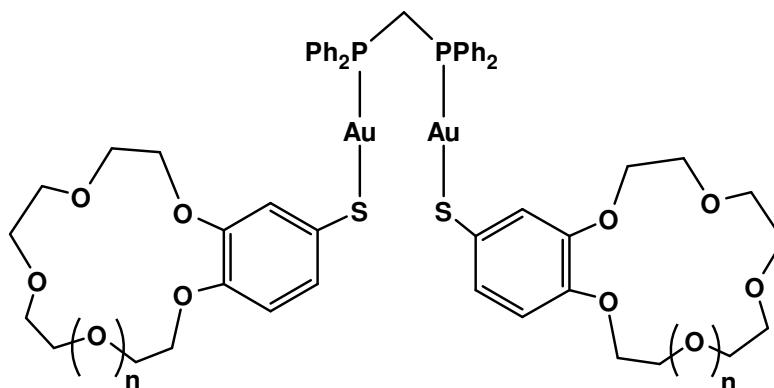


Figure 1.14. A gold(I)-based macrocycle for design of luminescent chemosensors and optoelectronic devices.

The existence of Au \cdots Au interactions have been observed in solution and in the solid-state. Studies revealing the formation of [2]catenanes,^[84] [2]rotaxanes^[85] and acid-base stacking^[86] in solution have been conducted. In the solid-state, research efforts have been much more exploratory in an effort to understand and control the emission. Some examples in this regard include an X-ray photocrystallographic analysis of the photoexcited charge-transferred state of [ClAu(PPh₃)₂] in a polymorphic crystal^[87] and a photoexcited intraligand (IL) or ligand-to-metal charge-transfer (LMCT) state from which the emission colours can be tuned through derivatized ligands.^[88-89] In a number of dinuclear gold(I) complexes the presence (or absence) of intermolecular Au \cdots Au interactions can be predicted solely based on an evaluation of the emission profile removing the need for X-ray studies.^[90]

In addition to auriphilic interactions, there are also other types of interesting metallophilic interactions of the type Au \cdots M (M = Ag, Tl, Cu). A spectacular example of emission control had been reported by Strasser and Catalano in a Au \cdots Cu cooperative system by creating a vapochromic material.^[19a] Understanding the excited states and factors governing excited state properties is essential for the eventual use of gold(I) complexes as sensors and molecular LEDs,^[91] as luminescence in gold(I) complexes can originate from ligands in certain geometries around the metal centre or be solely by the contribution of Au \cdots Au interactions.^[13a] Quite a number of perfluoroaryl complexes that had been prepared to date^[92a] and reviewed by Laguna *et al.*^[92b] Of note in these perfluoroaryl complexes is that they form an important aspect in gaining

a deeper understanding of the nature of photophysical properties associated with these gold(I) complexes, since the C₆F₅ unit by itself has been demonstrated by Zgierski *et al.* to quench luminescence and therefore emission in such as system must be attributed to the role of the metal, especially where Au...Au interactions are present.^[93]

In dinuclear gold(I) chemistry incorporating bis(phosphines), luminescence studies have been conducted by Fackler and co-workers on cationic systems such as [Au(dppm)]₂[BF₄]₂ and [Au(dppm)]₂Cl₂.^[94] Related cyclic dinuclear gold(I) complexes have been demonstrated by Eisenberg and co-workers to have immense potential to be used as sensors for VOCs, with changes in emission profiles upon exposure to VOC vapours.^[95]

In this study the dppm-CN ligand was used towards formation of its first gold(I) complexes, and there is interest in its structure and reactivity and luminescent properties.

1.1.6 Techniques for Characterization of Gold Phosphine Complexes

1.1.6.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

The use of NMR as a tool for analysis of gold phosphine based complexes is common, and amongst the ¹H, ¹³C and ³¹P NMR studies, it is the ³¹P NMR experiments that are often advantageous in studies of transitional-metal complexes compared to phosphine ligands. ³¹P NMR offers greater sensitivity in chemical shifts (chemical shift range in the order of 200 ppm) when comparing with the proton chemical shift range, which is in the order of 10-15 ppm.^[96] The symmetrical nature of most mono- and bis(phosphines) used in the coordination chemistry of gold makes most ³¹P NMR data to be interpreted simple due to the commonly observed sharp peaks that can be used quantitatively in analysis. In this thesis ³¹P NMR studies were used to study the dppm-CN and new gold(I) and copper(I) complexes and were used in conjunction with with ¹H and ¹³C NMR studies.

1.1.6.2 Single Crystal X-Ray Crystallography

Single crystal X-ray crystallography has become a routine analytical procedure in modern laboratories. The technique can be described as a method to search for the internal structure of a crystal with high accuracy, and to determine the atomic arrangements in space.^[97] The employment of this technique in gold chemistry had a pronounced effect in establishing the aurophilic effect regarding the packing arrangements of the gold atoms as a structural motif in the solid-state. Single crystal X-ray studies-represent and require high quality single crystals which can be formed by various established procedures. Section 1.1.1, the existence and differentiation of polymorphs in gold chemistry can readily be done using this powerful method. Crystallography can be used in aiding with the explanation of ambiguous results that may be obtained from spectroscopic techniques, such as infrared and NMR, and can prove to be a superior method of analysis, as results can be interpreted with the full knowledge of the structure of the complex. In this study this technique has been used to solve new gold(I) structures and in the determination of the structure of a gold(I) polymorph, a complex earlier described by Schmidbaur and co-workers.^[98]

1.1.6.3 Luminescence

Over the years luminescence techniques have proven to be an invaluable tool in analysis of a variety of compounds^[99] and have opened new possibilities into exploration of microscopic structure and the dynamics involved.^[100] The method depends upon excitation of the compound by radiation and upon relaxation of the species in the excited state, emission of light is observed. In gold(I) complexes luminescence can originate from Ligand-to-Metal Charge Transfer (LMCT) and *vice versa* (MLCT), or both with a contribution from the Au...Au interaction as noted in 1.1.5. As mentioned, the emission profiles can be used to determine if there are any Au...Au interactions present in the structure and in this manner the technique can be used as a qualitative tool.

1.2 Goals of the Study

The goals of this study can be summarized as follows:

- To make a comparison (based on the solid-state X-ray crystallographic studies), of the polymorphic complex which was isolated in a serendipitous manner, with the complex earlier described by Schmidbaur and co-workers.
- To synthesize and isolate the dppm-CN ligand by a modification of the reported synthetic route by Erker and co-workers that involves the deprotonation of the common chemical acetonitrile.
- To synthesize and characterize a number of new open-ended- and metallocyclic dinuclear gold(I) complexes using the dppm-CN ligand.
- To undertake a preliminary investigation of the luminescence properties and reactivity of the newly formed complexes.

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2

Experimental

2.1 General

Warning: The majority of organophosphorus compounds used in this study have a foul smell, flammable and toxic. Manipulations and materials described herein should be performed in a well-ventilated fume hood. Tetrahydrothiophene may cause conjunctivitis.

Unless otherwise noted, all reactions and manipulations were carried out in an inert atmosphere with a positive nitrogen gas flow (predried by a column of Drierite) using standard Schlenk techniques^[1] (in some instances Argon gas was used). Solutions were stirred magnetically with a Teflon-coated stirrer-bar. Room temperature refers to 24-26 °C. Glassware were oven dried for a 24-hour period at ~200 °C prior to use and assembled while hot under nitrogen atmosphere. Temperatures of -78 °C were obtained by dissolving a block of dry ice in acetone.

2.2 Solvents, Gases and Reagents

All solvents were pre-dried before use. This was achieved by activating molecular sieves by heating them in a furnace at 300-450 °C overnight. The activated sieves were added to the solvents and allowed to stand for a period of three days. All solvents were freshly distilled and used immediately. Diethyl ether, toluene, hexane and tetrahydrofuran (THF) were dried over sodium-benzophenone under nitrogen until the purple colour of the benzophenone-ketyl persisted. Dichloromethane (DCM) was dried over calcium hydride (CaH₂) under nitrogen prior to use, except in the instance of the preparation of the polymorph where it was used directly. Ethanol was dried over magnesium-iodine turnings. Solvents were freshly distilled before use, and all other reagents were synthetically pure.

Nitrogen, argon and ammonia gases were obtained from Afrox Limited Gas Co. Deuterated solvents were obtained from Sigma Aldrich Chemical Co. The preparation of starting materials are based on literature procedures and an outline is reported here as minor deviations were observed: $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$, $[\text{AuCl}(\text{tht})]$,^[2] $[\text{AuC}_6\text{F}_5(\text{tht})]$,^[2] $[\text{AuClPPh}_3]$,^[2] $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$,^[3] $[(\text{ClAu})_2\text{dppm}]$,^[4] $[(\text{ClAu})_2\text{dppe}]$,^[5] $[(\text{ClAu})_2\text{dpph}]$ ^[6] and $[(\text{ClAu})_2\text{dppb}]$.^[7] Acetonitrile was dried over CaH_2 and freshly distilled before use. The following chemicals were purchased from Aldrich Chemical Co. and were used as received: chlorodiphenylphosphine (ClPPh_2) 98%, n-butyllithium solution, 1.6 M in hexane, and 2.5 M in hexane, tetrahydrothiophene 99%, hexafluorophosphoric acid 60 wt % solution in water (HPF_6) and phosphorus pentasulfide 99%. Gold solution [pre-dissolved in aqua regia ($3\text{HCl} : 1\text{HNO}_3$)] was used as basis in preparation of all gold(I) starting materials and was a generous gift from Rand Refineries.

2.3 Instrumentation

2.3.1 Melting Points

All melting points were measured on a Bibby Stuart Scientific Model SMP3 apparatus (United Kingdom). All measurements are expressed in degrees Celsius ($^{\circ}\text{C}$) and are uncorrected.

2.3.2 Elemental Analysis

All elemental microanalyses were obtained using a Leco CHNS-932 micro-elemental analyzer, Instrumental laboratory, UKZN.

2.3.3 Nuclear Magnetic Resonance (NMR)

NMR spectra were obtained on a Bruker 400 MHz spectrometer. Deuterated chloroform (CDCl_3), Toluene- d_8 and Dimethylsulfoxide (DMSO) were used as solvents. ^1H and ^{13}C NMR data are expressed in parts per million (ppm) and as chemical shifts position (δ_{H}): (**s** = singlet; **d** = doublet; **dd** = doublet of doublets; **t** = triplet; **tt** = triplet of triplets; **p** = pentet; **sx** = sextet and **m** = multiplet), **br** = broad, relative integral, assignment, and coupling constant, J/Hz (if

applicable). $^{31}\text{P}\{^1\text{H}\}$ spectra were obtained on a Bruker 400 MHz spectrometer, with chemical shifts reported relative to a 85% H_3PO_4 in D_2O external standard solution.

2.3.4 Infrared (IR)

Infrared spectra were obtained on a FT-IR Perkin Elmer Spectrometer, Model RX 1. All characteristic peaks are reported in wavenumbers (cm^{-1}) in the range 4000-400 cm^{-1} . A homogeneous potassium bromide (KBr) pellet was used for the analysis of some compounds that were obtained in powder form. A FT-IR Perkin Elmer Spectrometer, Model 100 equipped with Universal ATR Sampling Accessory was used to analyse compounds obtained as powders whenever KBr disks were not used, (**w** = weak, **m** = medium, **s** = strong, **vs** = very strong, **br** = broad).

2.3.5 X-ray crystallography

Data was collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO^[8] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software^[9] and refined using SAINT on all observed reflections.

Data reduction was performed using SAINT software^[10] which corrects for Lp. Scaling and absorption corrections were applied using SADABS^[11] multi-scan technique, supplied by George Sheldrick. The structures were solved by direct methods using the SHELXS-97 program and refined by least squares method on F^2 , SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.^[12] All non-hydrogen atoms are refined anisotropically and hydrogens calculated by geometrical methods and refined as a riding model.

The Flack^[13] parameter was used to determine chirality of the crystal studied, the value should be near zero, a value of one is the other enantiomer and a value of 0.5 is racemic. All the crystals used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

2.3.6 Luminescence Studies

An emission spectrum of **3** was recorded using a Photon Technologies Int. (PTI) fluorescence spectrometer controlled by PTI's Felix32© Version 1.1 Software.^[14] A quartz NMR tube served as the solid sample holder. Steady state emission spectra were recorded using PTI's XenoFlashTM 300 Hz pulsed light source and gated emission scans with a delay of 95 μ s, an integration window time of 100 μ s and 50 pulses per channel (shots). Detection was by means of PTI's Model 814 Analog/Photon-Counting Photomultiplier Detector. The excitation wavelength was 250 nm for the sample; with the scattered light being removed by means of a suitable wavelength bandpass filter. The intensities (peak-heights) of the emission maxima were recorded at room temperature and the spectrum is uncorrected from instrument response.

2.4 Preparation of gold(I) and copper(I) starting materials.

2.4.1 Preparation of H[AuCl₄] \cdot 3H₂O

A solution [gold metal dissolved in aqua regia (3HCl: 1HNO₃)] (11 mL) was poured into a beaker and then diluted with deionised water to a 150 mL mark. The diluted solution was heated at constant temperature (90 °C) while stirring and the volume reduced to less than a quarter of the original volume. Heat was reduced to 35 °C and the solution reduced slowly to almost dryness while stirring. The residual content was allowed to cool to room temperature for a period of 10 minutes. The bright orange crystals of H[AuCl₄] \cdot 3H₂O were collected and the mass and weighed. Yield: (7.66 g).

2.4.2 Preparation of $[\text{AuCl}(\text{tht})]^{[2]}$

To a beaker (250 mL) was added freshly prepared $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ (7.66 g, 0.0194 mol) and this was dissolved with $\text{EtOH}/\text{H}_2\text{O}$ solvent (9:1 v/v) and the solution stirred continuously. To this solution, tht was added dropwise and the solution formed a yellow precipitate $[\text{AuCl}_3(\text{tht})]$. With continuous stirring more tht was added until a white precipitate was obtained. The addition of tht was ceased and the white precipitate collected through filtration and the product washed with portions of cold EtOH (3 x 5 mL). The product was obtained as a free flowing white powder, and was placed in a vial after purging with nitrogen gas and placed in the fridge for further use. Yield: (5.76 g, 0.0180 mol) 92%.

2.4.3 Preparation of $[\text{AuC}_6\text{F}_5(\text{tht})]^{[2]}$

A Schlenk flask equipped with a magnetic stirrer bar was charged with Et_2O (35 mL) and the flask cooled to $-78\text{ }^\circ\text{C}$ in a dry-ice/acetone bath. To the cooled flask was slowly added $\text{C}_6\text{F}_5\text{Br}$ (0.95 mL, 7.5 mmol) by means of an airtight syringe and the mixture stirred for 5 minutes. To this solution, $n\text{BuLi}$ (1.6 M, 4.7 mL, 7.5 mmol) was added by a syringe at a rate of 1 drop per sec while continuously stirring. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 hour, after this $[\text{AuCl}(\text{tht})]$ (1.56 g, 4.85 mmol) was added followed by the addition of Et_2O (40 mL) to the reaction flask and the reaction stirred further for 15 minutes.

The solution was allowed to warm up gently to $-30\text{ }^\circ\text{C}$ over a period of 1 hour, and then removed from the cold source and allowed to reach room temperature and stirred for a further 45 minutes. To the white precipitate formed, were added 5 drops of deionised water and the mixture filtered over anhydrous MgSO_4 . The filtrate was concentrated to a volume of 10 mL and this was followed by the addition of hexane (15 mL) to precipitate the product. All of the solvent was removed under reduced pressure and the product obtained as a free flowing white powder. Yield: (1.76 g, 3.91 mmol) 80%.

2.4.4 Preparation of [AuClPPh₃]^[2]

A Schlenk flask equipped with a magnetic stirrer was charged with [AuCl(tht)] (300 mg, 0.94 mmol) and this was dissolved in DCM (5 mL). Another Schlenk flask was charged with PPh₃ (240 mg, 0.94 mmol) and this was also dissolved in DCM (7 mL). The gold(I) solution was added in one portion to the PPh₃ solution and the final mixture stirred at room temperature for a period of 30 minutes. All of the solvent and tht were removed, and then portions of Et₂O added to further dry the product. The product was isolated as a free flowing powder. Yield: (350 mg, 0.700 mmol) 75%.

2.4.5 Preparation of [Cu(CH₃CN)][PF₆]^[3]

A Schlenk flask equipped with a magnetic stirrer bar was charged with Cu₂O (1.01 g, 7.08 mmol, 1 mol equiv.) and this was suspended by the addition of acetonitrile (20 mL) while stirring. To the formed suspension was added HPF₆ (2.5 mL, 28.3 mmol, 4 mol equiv.) dropwise, and stirred until most of the Cu₂O material was dissolved. The clear solution was then filtered through a hot porosity frit and the frit washed with small portions of acetonitrile (3 x 2 mL). The solution was stirred for 2 minutes and then Et₂O (25 mL) added to precipitate the product and then the mixture cooled for 3 hrs at 0 °C to further induce precipitation. The product was collected by filtration and the product washed with portions of cold Et₂O (2 x 3 mL). The product was obtained as a white-microcrystalline material, purged and stored in the fridge until further use. Yield: (2.55 g, 6.80 mmol) 96%.

2.4.6 Preparation of [(ClAu)₂(dppm)]^[4]

A Schlenk flask equipped with a magnetic stirrer bar was charged with dppm (100 mg, 0.240 mmol, 1 mol equiv.) and dissolved in DCM (5 mL). To another Schlenk flask was added [ClAu(tht)] (156 mg, 0.48 mmol, 2 mol equiv) and dissolved in DCM solvent (8 mL). The gold(I) mixture was poured to the ligand solution in one portion and the mixture stirred at room temperature for a period of 15 minutes. All of the solvent and tht was removed and the product dried further by addition and removal Et₂O under reduced pressure. The product was isolated as

a free-flowing white powder. Yield: (197 mg, 0.23 mmol) 96%.

2.4.7 Preparation of [(ClAu)₂(dppe)]^[5]

See Section 2.4.6 for procedure, dppe (203 mg, 0.510 mmol, 1 mol equiv) and [ClAu(tht)] (327 mg, 1.02 mmol, 2 mol equiv). Yield: (427 mg, 0.490 mmol) 96%.

2.4.8 Preparation of [(ClAu)₂(dpph)]^[6]

See Section 2.4.6 for procedure, dpph (240 mg, 0.530 mmol, 1 mol equiv) and [ClAu(tht)] (338 mg, 1.06 mmol, 2 mol equiv). Yield: (402 mg, 0.490 mmol) 82%.

2.4.7 Preparation of [(ClAu)₂(dppb)]^[7]

See Section 2.4.6 for procedure, dppb (306 mg, 0.720 mmol, 1 mol equiv) and [ClAu(tht)] (460 mg, 1.43 mmol, 2 mol equiv). Yield: (571 mg, 0.640 mmol) 89%.

2.5 Preparation of complex [(ClAu){PPh₂(OH)}], (1)

A Schlenk flask equipped with a magnetic stirrer bar was charged with wet DCM (5 mL) and this was followed by addition of ClPPh₂ (0.210 mL, 1.11 mmol) and the mixture stirred for 20 minutes at room temperature. A DCM solution of [AuCl(tht)] (354 mg, 1.11 mmol) was added in one portion and the resulting mixture stirred for a further 15 minutes. All of the solvent and tht were removed and the product isolated as a free-flowing white powder. ³¹P NMR (101 MHz, CDCl₃, 298 K) δ_P = 89.2 (s, 1P). X-Ray crystal structure analysis for C₁₂H₁₁AuClOP (1). Single crystals were obtained by slow diffusion of hexane vapor into a saturated solution of 1 in dichloromethane.

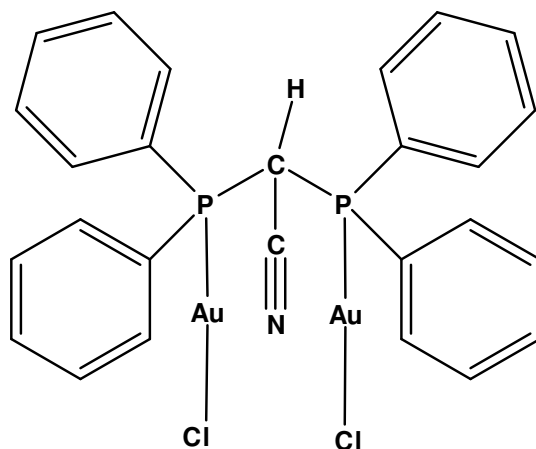
2.5 Preparation of the dppm-CN ligand (2)

The synthesis of the di(phenylphosphino)acetonitrile dppm-CN ligand is based on a modified procedure by Braun *et al.*^[15]

To a Schlenk flask (150 mL) equipped with a magnetic stirrer bar was added THF (~ 10 mL). To this was added acetonitrile (0.21 mL, 4 mmol, 1 mol equiv, dried and distilled from CaH₂). The flask was cooled to -78 °C and then n-butyllithium (5 mL, 8 mmol, 1.6 M, 2 mol equiv.) added dropwise while stirring over a period of 10 minutes. The clear solution was stirred in the cold for a period of 30 minutes and no suspension formed at this time. After this period the solution has turned slightly yellow in colour. To this cold solution (-78 °C) was added ClPPh₂ (1.48 mL, 8 mmol, 2 equiv., diluted with minimal THF before addition) slowly while stirring. The solution turned blood-red in colour. The solution was stirred at this temperature for a period of 15 minutes and then allowed to warm up to room temperature to which it was stirred for a further 10 minutes; the solvent was removed in *vacuo*. To the residue was added DCM (30 mL) and the precipitated LiCl removed by filtration over Celite/ anhydrous MgSO₄ composite, the solid was then washed with DCM (2 x 15 mL).

The filtrate was concentrated to a volume of ~5 mL and then dry ethanol (1 x 40 mL) added. The solution was stirred while the product precipitated. The solid off-white product (**2**) was dried in *vacuo*. Yield: (1.62 g, 3.96 mmol) 52 %; Mp: 135-138 °C (142 °C literature); ¹H NMR (400 MHz, CDCl₃, 298 K) $\delta_{\text{H}} = 7.49\text{-}7.28$ (m, 20H, Ph); 3.80 (t, 1H; CH, ²J_{P,H} = 3.52 Hz); ¹³C NMR (101 MHz, CDCl₃, 298 K) $\delta_{\text{C}} = 134.2, 132.9, 129.9, 128.8, 34.2$ ³¹P NMR (101 MHz, CDCl₃, 298 K) $\delta_{\text{P}} = -10.1$ (s, 2P); IR: (KBr, cm⁻¹): 2227 (vs, CN).

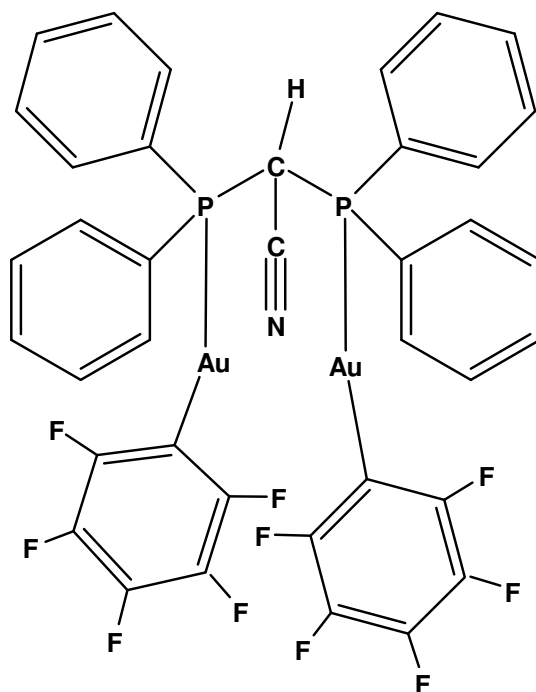
2.6 Preparation of the [(ClAu)₂(dppm-CN)] complex (**3**)



To a small Schlenk flask (50 mL) equipped with a magnetic stirrer bar was added (**2**) (100.1 mg, 0.24 mmol, 1 mol equiv) and this was dissolved in DCM (5 mL). To another small Schlenk flask was added [AuCl(tht)] (156 mg, 0.48 mmol, 2 mol equiv) and this was also dissolved in DCM (10 mL). To the clear solution of (**2**) was added the solution of [AuCl(tht)] in one portion while stirring. The resulting solution was stirred further for 45 minutes at room temperature. All of the solvent and tht were removed under reduced pressure to give complex **3**. Dry Et₂O (3 x 2 mL) was added to wash the product which was further dried in *vacuo* overnight.

The product was obtained as a free flowing off-white powder. Yield: (185 mg, 0.21 mmol) 88%; Mp: 155-158 °C (decompose); Elemental analysis for complex C₂₆H₂₁Au₂Cl₂NP₂ found: C 35.21, H 2.28 requires: C 35.72, H 2.42; ¹H NMR (400 MHz, CDCl₃, 298 K) δ_H = 7.68-7.53 (m, 20H, Ph); 5.52 (t, 1H; CH, ²J_{P,H} = 12.77 Hz). ¹³C NMR (101 MHz, CDCl₃, 298 K) δ_C = 135.8, 133.8, 133.0, 132.8, 129.8, 30.81. ³¹P NMR (101 MHz, CDCl₃, 298 K) δ_P = 34.8 (s, 2P); IR (KBr, cm⁻¹): 2243 (s, CN). ESI-MS: m/z 875 [M⁺]. X-Ray crystal structure analysis for C₂₆H₂₁Au₂Cl₂NP₂ (**3**). Single crystals were obtained by slow diffusion of hexane vapor into a saturated solution of **3** in dichloromethane.

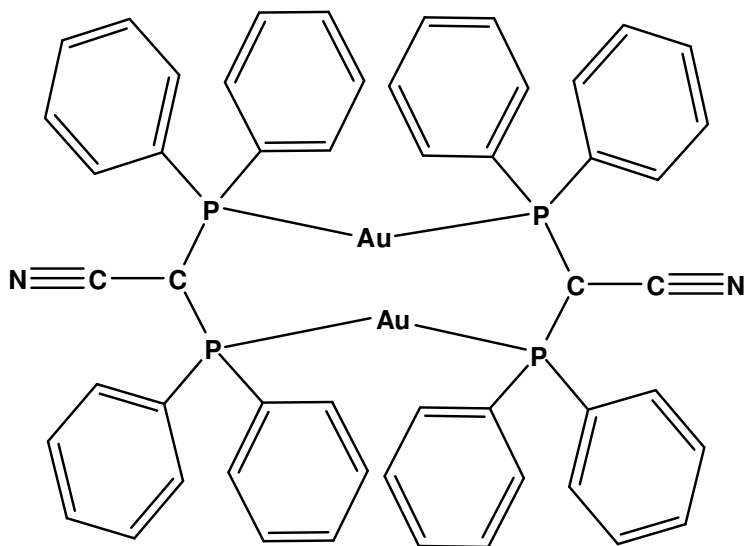
2.7 Preparation of the $[(C_6F_5Au)_2(dppm-CN)]$ complex (**4**)



To a 50 mL Schlenk flask equipped with a magnetic stirrer bar was added (**2**) (101.5 mg, 0.24 mmol, 1 mol equiv) and this was dissolved in DCM (3 mL). To another small Schlenk flask was added $[AuC_6F_5(tht)]$ (220.94 mg, 0.48 mmol, 2 mol equiv) and this was also dissolved in DCM (10 mL). To the clear solution of (**2**) was added the solution of $[C_6F_5Au(tht)]$ in one portion and the resulting solution stirred for 15 minutes at room temperature. All of the solvent and tht were removed under reduced pressure to obtain complex **4**. To wash the product, dry EtOH (1 x 2 mL) was added and then dried further in *vacuo* overnight. The product was obtained as a free-flowing pale-yellow powder. Yield: (227 mg, 0.20 mmol) 83 %; Mp: 115-117 °C (decompose); Elemental analysis for complex $C_{38}H_{21}Au_2F_{10}NP_2$ Found: C, 39.94, H, 2.11, N, 1.12 requires C, 40.13, H 1.86, N 1.23. 1H NMR (400 MHz, $CDCl_3$, 298 K) δ_H = 7.88-7.82 (m, 20H; Ph) 4.71 (t, 1H; CH, $^1J_{P,H}$ = 10.85 Hz); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ_C = 135.7, 133.2, 129.8.0, 129.5, 65.8, 15.2. ^{31}P NMR (101 MHz, $CDCl_3$, 298 K) δ_P = 42.0 (s, 2P); IR (KBr, cm^{-1}): 2137 (s, CN). ESI-MS: m/z 1138 $[M+]$. X-Ray crystal structure analysis for $C_{38}H_{21}Au_2F_{10}NP_2$ (**4**)

Single crystals were obtained by slow diffusion of hexane vapor into a saturated solution of **4** in dichloromethane.

2.8 Preparation of the $[\text{Au}_2\{(\text{PPh}_2)\text{CCN}\}]$ complex (**5**)

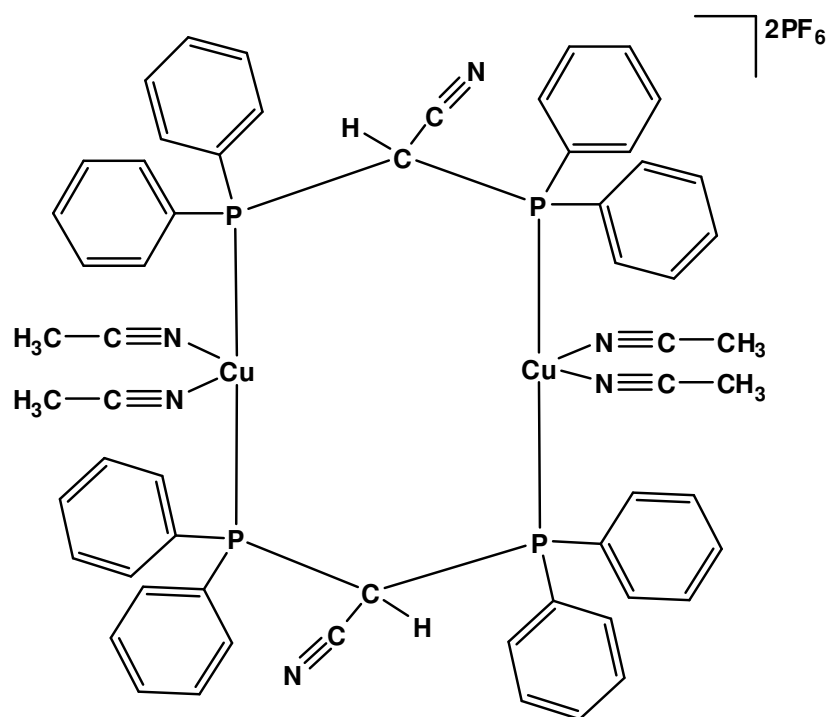


A Schlenk flask (50 mL) equipped with a magnetic stirrer bar was charged with (**2**) (700 mg, 1.71 mmol, 1 mol equiv) and this was dissolved in THF (10 mL). The prepared solution was cooled to $-78\text{ }^\circ\text{C}$ and then ${}^n\text{BuLi}$ (2.5 M, 0.70 mL, 1.71 mmol, 1 mol equiv) added dropwise and the resulting solution stirred for 30 min. Another Schlenk flask (20 mL) equipped with a magnetic stirrer bar was charged with $[\text{ClAu}(\text{tht})]$ (548 mg, 1.71 mmol, 1 mol equiv) dissolved in THF (10 mL), this solution was slowly added to the lithiated dppmCN.

The resulting solution was stirred at $-78\text{ }^\circ\text{C}$ for 30 minutes and the solution allowed to reach room temperature and then stirred further for 15 minutes. All of the solvent and tht were removed under reduced pressure and the product extracted with DCM by stirring the solution for at least 30 minutes. The precipitated LiCl salt was filtered off and the solvent removed under

reduced pressure. The product was dried further in *vacuo* for 2 hrs. The product (**5**) was obtained as a free flowing light-yellow powder. Yield: (960 mg, 0.79 mmol) 92%. Mp: 200-205 °C (decompose); Elemental analysis for complex $C_{52}H_{40}Au_2N_2P_4$ Found: C 51.19, H 3.18, N 2.19 requires C, 51.59; H, 3.33; N, 2.31. 1H NMR (400 MHz, $CDCl_3$, 298 K) $\delta_H = 7.55-7.42$ (m, 40H, Ph); ^{31}P NMR (101 MHz, $CDCl_3$, 298 K) $\delta_P = 42.8$ (s, 2P), IR (ATR, cm^{-1}): 2133 (s, CN). X-Ray crystal structure analysis for $C_{52}H_{40}Au_2N_2P_4$ (**5**). Single crystals were obtained by slow diffusion of hexane vapor into a saturated solution of **5** in dichloromethane.

2.9 Preparation of $[(Cu)_2(dppmCN)_2(CH_3CN)_4][PF_6]_2$ complex (**6**)



To a Schlenk flask (50 mL) equipped with a magnetic stirrer bar was added (**2**) (100 mg, 0.24 mmol, 1 mol equiv) and this was dissolved in DCM (5 mL). To another Schlenk flask was added $[Cu(CH_3CN)_4][PF_6]$ (91.1 mg, 0.24 mmol, 1 mol equiv) and this was also dissolved in DCM (8 mL). The $[Cu(CH_3CN)_4][PF_6]$ solution was added to the solution of dppm-CN in one portion and

the mixture stirred for a period of 30 min at room temperature. After the reaction period, all of the solvents were removed and the product (**6**), obtained as free-flowing off white powder, was isolated. Yield: (137 mg, 0.098 mmol) 82%; Mp: 209-210 °C; Elemental analysis for complex $C_{60}H_{54}Cu_2F_{12}N_6P_6$ Found: C, 51.69, H, 3.82, requires C, 51.47, H, 3.89; ^{31}P NMR (101 MHz, $CDCl_3$, 298 K) $\delta_P = 42.4$ (s, 2P), from -135 to -152 (PF_6). IR (KBr, cm^{-1}): 2230, 2161 (s, CN).

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3

Neutral Open-ended and Metallacyclic Dinuclear Gold(I) Complexes of dppm-CN

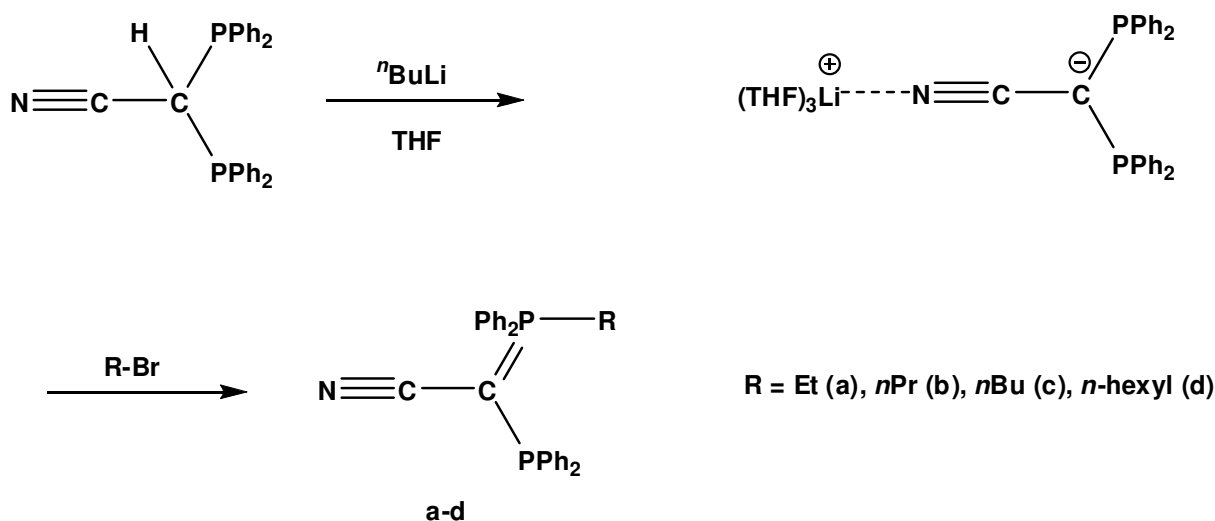
3.1 Introduction and Goals of Study

The emphasis on this chapter will be largely based on the synthesis and characterization of new gold(I) complexes of dppm-CN and is preceded by a comparison of a polymorphic compound, **1**, (isolated serendipitously), with a complex the described in literature by Schmidbaur and co-workers.

The formation of different polymorphic forms has a remarkable effect in terms of structure and properties of the material.^[1] A special interest is shown in the gold(I) type of complexes where the concept of aurophilicity is used towards manipulation of structure and thus aiding the process of design of polymorphic materials for finding application in various fields (Chapter 1, Section 1.1.1). In this dissertation a second polymorph of the complex $[(\text{ClAu})\{\text{PPh}_2(\text{OH})\}]$ earlier reported by Schmidbaur and co-workers,^[2] was isolated and structurally characterized.

The role of functionalized bis(phosphines) in the development of the coordination chemistry of transition metals is useful. This is shown, for example, in the use of bis(diphenylphosphino)amine (PNP) ligands in chromium catalysed ethylene tri- and tetramerization reactions reported by Bercaw and co-workers,^[3] in the preparation of heteroselenometallic clusters,^[4] and in the preparation of rare Mo(II) complexes.^[5] The pronounced effect that the PNP ligand has shown in its ability to stabilizing reactive intermediates which is not present in the commonly used dppm ligand.^[3] A classical example of the use of functionalized bis(phosphines) is the use of the bis(diphenylphosphino)pyridine ligand by Balch and co-workers in the design of complexes of Pd(II) and Pt(II) with a designed space between two metal centers.^[6] The implication of using systems different from the common

dppm, is the effect of an additional functional group that allows for changes in structure and reactivity. The development of dppm-CN (Chapter 1, Section 1.1.3) as a versatile ligand in coordination chemistry needs further investigation,^[7] and this includes reactivity studies of the lithiated dppm-CN towards alkylation and the formation of various phosphorus ylides (Scheme 3.1).



Scheme 3.1. Development of the dppm-CN ligand by Erker and co-workers through formation of phosphorus ylides.

As mentioned before, the chemistry of the ligand dppm-CN has been rejuvenated through a new synthetic route reported by Erker and co-workers.^[8] This study reports the first use of the ligand in molecular gold(I) complexes and an investigation with regard to its structure and luminescent properties.

In this study the dppm-CN ligand was synthesized by modification of a procedure involving double deprotonation of acetonitrile and alteration of reaction times and conditions. The ligand generated open-ended and cyclic dinuclear gold(I) complexes whereby the role of the coordination mode of dppm-CN in the bridging mode opened the possibility of investigating new potential reactivity trends of the cyano functional group.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization

3.2.1.1 A New Polymorph of [(ClAu){PPh₂(OH)}] (1)

The formation of complex **1** as a polymorph was serendipitous, and included isolation after a reaction between diphenylphosphinous acid and a gold(I) starting material in wet DCM. A ³¹P NMR study showed a sharp singlet at $\delta = 89.5$ for **1** which corresponds well with the value of $\delta = 90.4$ for its polymorph reported in literature. Since polymorphs must have the same resonance in solution, and since the same solvent (CDCl₃) was used in both cases, the small difference (0.9 ppm) is ascribed to possible difference in temperature during data acquisition.

An X-ray crystallographic study revealed that the polymorph can be considered a dimer (Fig. 3.1) that crystallizes in the C2/c space group (monoclinic) and the monomeric units are held together by Au...Au interactions of 3.0375(2) Å. The Au...Au separation in **1** is shorter than the corresponding polymorph reported in literature (triclinic) which has a distance of 3.1112(7) Å. Based on the current studies, it cannot readily be inferred whether the polymorph with the shorter Au...Au interactions is the thermodynamically more stable of the two.

The Au(1)-Cl(1) bond length in **1** is longer at 2.3366(9) Å, relative to that of the triclinic polymorph at 2.306(2) Å, although the Au(2)-P(2) bond length in **1** is 2.2254(10) Å is almost identical to that of the polymorph at 2.224(2) Å. The P(1)-O(1) in **1** is 1.592(3) Å versus 1.597(5) Å in the triclinic polymorph. In complex **1** there are peripheral O-H...Cl hydrogen bonds in addition to the Au...Au interactions forming the dimer similar to the triclinic polymorph. The O-H...Cl(2) interaction in complex **1** has a bond angle of 169.9° compared to the similar angle of 165.6° in the triclinic polymorph. The Cl(1)-Au(1)-P(1) = 179.23(3)° bond angle is linear whilst the Cl(2)-Au(2)-P(2) = 170.39(4)° bond angle is significantly more distorted from linearity. The latter Cl-Au-P unit can be compared to both the Cl-Au-P angles in the triclinic polymorph, which are at 169.18(7)° and 170.85(7)°, respectively, i.e. both deviate from linearity. The possible cause for which the Cl(1)-Au(1)-P(1) and Cl(2)-Au(2)-P(2) are

different from each other has to do with orientation of the two limbs. The interaction of the Cl(1) atom, is far from the O(2)-H(2) group such that there is very little or no hydrogen bonding. The Cl(2) atom on the other hand, is closer to the O(1)-H(1) such that there is significant hydrogen bonding between two units, and thus responsible for the observed differences and distortion of the Cl(2)-Au(2)-P(2) unit. In the triclinic polymorph described in literature, hydrogen bonding is present on both monomeric units leading to significant distortion from linearity.

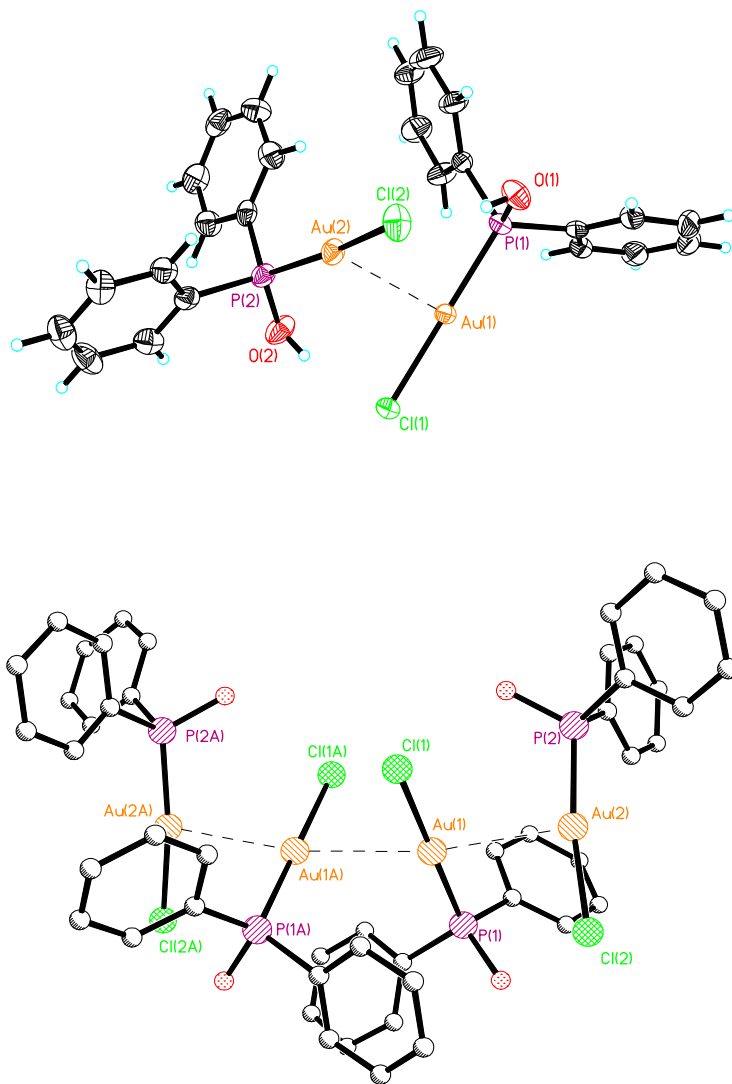


Figure 3.1. Above: Molecular structure of (1) with relevant atom labelling shown. Drawn at 50% probability level. Below: Propagation of Au···Au interactions at distances of 3.0374(2) Å and 3.0112(3) Å.

Table 3.1. Crystal data and structure refinement for complex (1)

Empirical formula	C ₁₂ H ₁₁ AuClOP	
Formula weight	434.59	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.2734(18) Å	α = 90°.
	b = 10.2321(6) Å	β = 106.4830(10)°.
	c = 17.5643(11) Å	γ = 90°.
Volume	5044.8(5) Å ³	
Z	16	
Density (calculated)	2.289 Mg/m ³	
Absorption coefficient	11.978 mm ⁻¹	
F(000)	3232	
Crystal size	0.32 x 0.13 x 0.06 mm ³	
Theta range for data collection	2.12 to 25.39°.	
Index ranges	-35 ≤ h ≤ 35, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21	
Reflections collected	18295	
Independent reflections	4651 [R(int) = 0.0361]	
Completeness to theta = 25.39°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.3707	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4651 / 0 / 291	
Goodness-of-fit on F ²	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0194, wR2 = 0.0463	
R indices (all data)	R1 = 0.0233, wR2 = 0.0479	
Largest diff. peak and hole	0.741 and -0.633 e.Å ⁻³	

Table 3.2. Selected bond lengths (Å) and angles (°) for complex **(1)**

Au(1)-P(1)	2.2304(10)	Au(1)-Cl(1)	2.3366(9)
Au(1)-Au(1)#1	3.0112(3)	Au(1)-Au(2)	3.0375(2)
Au(2)-P(2)	2.2254(10)	Au(2)-Cl(2)	2.3131(10)
P(1)-O(1)	1.591(3)	P(1)-C(1)	1.808(4)
P(1)-C(7)	1.808(4)	P(2)-O(2)	1.592(3)
<hr/>			
P(1)-Au(1)-Cl(1)	179.23(3)	P(1)-Au(1)-Au(1)#1	98.95(3)
Cl(1)-Au(1)-Au(1)#1	81.37(2)	P(1)-Au(1)-Au(2)	91.08(3)
Cl(1)-Au(1)-Au(2)	88.65(2)	Au(1)#1-Au(1)-Au(2)	169.256(4)
P(2)-Au(2)-Cl(2)	170.39(4)	P(2)-Au(2)-Au(1)	97.58(3)
Cl(2)-Au(2)-Au(1)	91.41(3)	O(1)-P(1)-C(1)	105.59(17)
O(1)-P(1)-C(7)	101.93(16)	C(1)-P(1)-C(7)	106.06(17)
O(1)-P(1)-Au(1)	115.24(11)	C(1)-P(1)-Au(1)	112.00(12)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+1/2

The packing arrangement in the crystal lattice as viewed along the a-axis (Fig. 3.2) show that in complex **1** the Au...Au interactions contains 8 dimers (Z=16) in a unit cell, whilst in the triclinic polymorph the packing show only 2 dimers (Z=4) per unit cell. The differences in packing forces through weak inter- and intramolecular interactions (hydrogen bonding and aurophilic interactions) are most likely the key factors producing different polymorphs; it would be of interest to discover whether these differences can also be observed in their respective solid state emission profiles (not part of the present study).

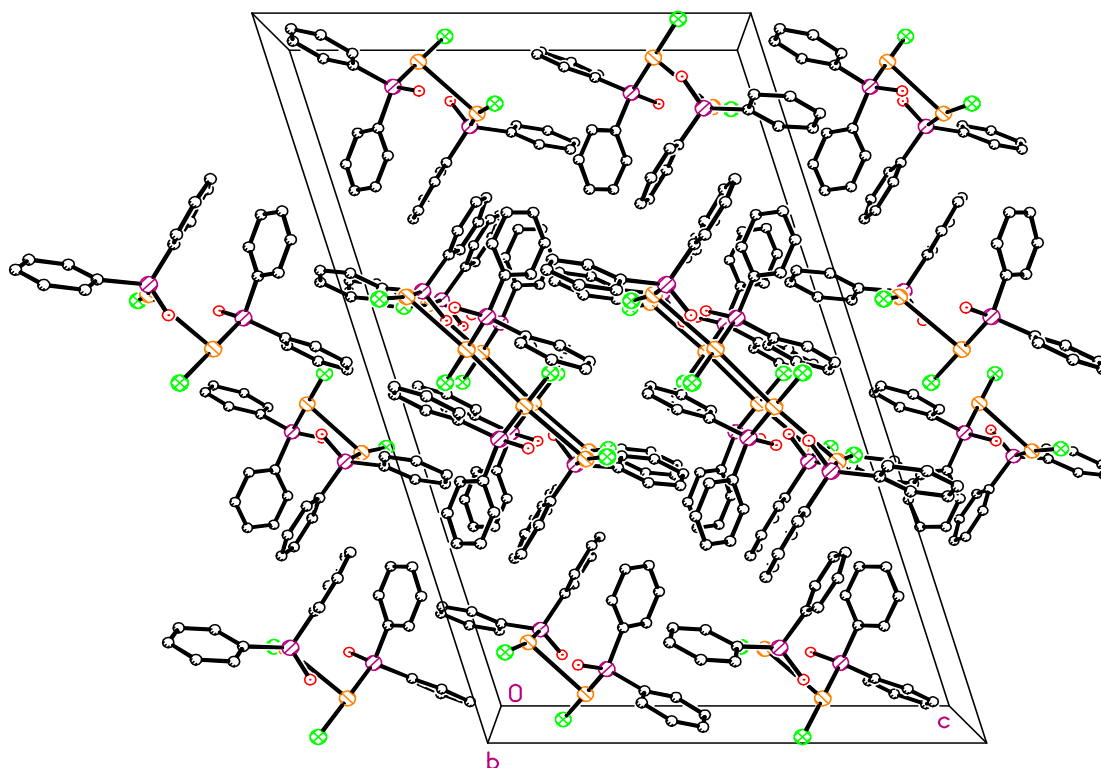


Figure 3.2. Crystal packing arrangement for unit cell of **(1)** as viewed along the a-axis.

3.2.2 Open-ended and cyclic gold(I) complexes from of dppm-CN

3.2.2.1 The open-ended $[(\text{ClAu})_2(\text{dppm-CN})]$ Complex (**3**)

The formation of new gold(I) complexes depended upon the preparation of the ligand **2**, obtained through the modification of the stoichiometric amounts used in the literature procedure.^[7] Acetonitrile was doubly deprotonated with $n\text{BuLi}$ (2 mol equiv.) to yield the proposed intermediate $\text{Li}_2[\text{CHCN}]$ (not isolated), which was treated *in situ* with Ph_2PCl (2 mol equiv.) to form ligand **2** in reasonable yields (52%) with similar yields reported (51%) in literature. The

ligand was characterized by several spectroscopic techniques with all the results corresponding with those reported in literature.

The formation of the complex [(ClAu)₂dppm-CN], **3**, followed from the treatment of dppm-CN with [ClAu(tht)] in DCM (1:2) and was isolated in high yields. Coordination of the bridging phosphine to Au(I) was evident from the solution ³¹P NMR of **3** that featured a main resonance at $\delta = +34.8$ for two equivalent P atoms. This peak is shifted considerably downfield when compared with the mononuclear chelating [(Cl₂M)(dppm-CN)] type complexes [M = Pd ($\delta = -33.8$) and Pt ($\delta = -44.6$)].^[8c]

The ¹H NMR C-H (bridging) resonance at $\delta = 5.52$ (²J_{PH} = 12.77 Hz, 1H) that split into a binomial triplet by a pair of equivalent adjacent ³¹P nuclei, and is shifted upfield compared to the triplet in the free ligand with C-H (bridging) resonance at 3.80 ppm. The IR spectrum showed a sharp peak at 2243 cm⁻¹, assigned to the cyano stretching mode.^[8a] The purity of the product was verified by subjecting complex **3** to elemental analysis and mass spectrometry (M⁺ ion peak = 874), both were in accord with the expected results.

The solid-state structure of **3** was verified by an X-ray crystallographic study (Fig. 3.3) and was recently published.^[9a] Complex **3** has an intramolecular Au...Au interaction of 3.1669(4) Å, but no intermolecular interaction. The P-C_{Ph} bond length is shorter at 1.810(7) Å than the P-C bond length at 1.876(7) Å for the bridging carbon.

The C-C≡N moiety is a linear 179.5° and the C≡N bond at 1.125(11) Å agrees well with the literature value for the free ligand at 1.148(3) Å.^[8a] Both the P-Au-Cl moieties are slightly distorted from linearity with the values of P(1)-Au(1)-Cl(1) = 176.84(7)° and P(2)-Au(2)-Cl(2) = 175.21(8)°. The geometry of the sp³ hybridized bridging-carbon P(2)-C(1)-P(1) is tetrahedral at 109.7(4)°.

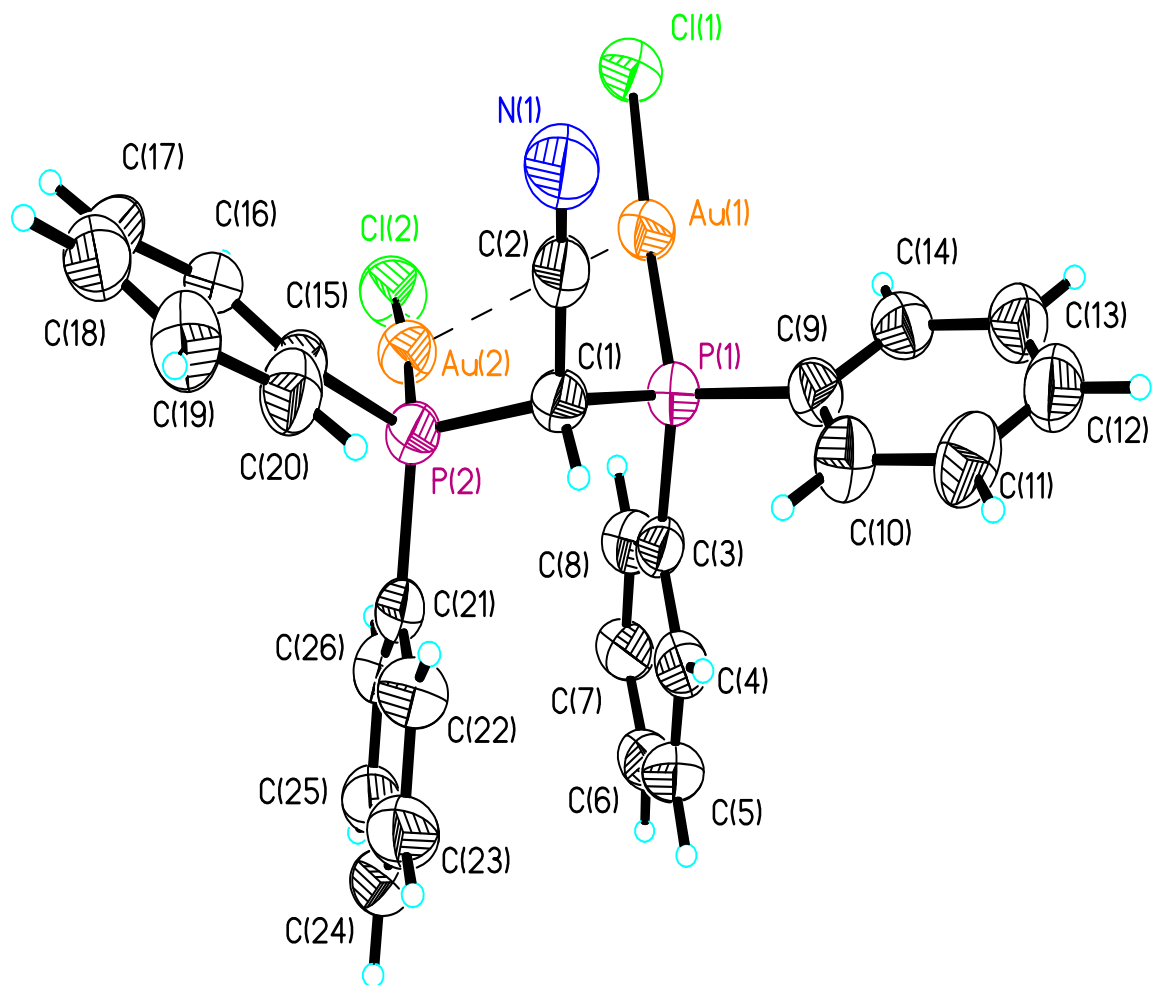


Figure 3.3. Molecular structure of **(3)** showing atom labelling scheme. Hydrogen atoms are shown. Drawn at 50% probability level.

Table 3.3. Crystal data and structure refinement for complex (3)

Empirical formula	$C_{26}H_{21}Au_2Cl_2NP_2$	
Formula weight	874.21	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	$a = 13.9062(8)$ Å	$\alpha = 90^\circ$.
	$b = 12.6837(7)$ Å	$\beta = 90^\circ$.
	$c = 14.7938(8)$ Å	$\gamma = 90^\circ$.
Volume	$2609.4(3)$ Å ³	
Z	4	
Density (calculated)	2.225 Mg/m ³	
Absorption coefficient	11.575 mm ⁻¹	
F(000)	1624	
Crystal size	$0.22 \times 0.21 \times 0.19$ mm ³	
Theta range for data collection	2.11 to 25.35°	
Index ranges	$-16 \leq h \leq 16$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$	
Reflections collected	35892	
Independent reflections	4770 [R(int) = 0.0594]	
Completeness to theta = 25.35°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2159 and 0.1889	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4770 / 1 / 298	
Goodness-of-fit on F ²	1.053	
Final R indices [I > 2sigma(I)]	R1 = 0.0249, wR2 = 0.0629	
R indices (all data)	R1 = 0.0257, wR2 = 0.0632	
Absolute structure parameter	0.014(8)	
Largest diff. peak and hole	0.757 and -0.812 e.Å ⁻³	

Table 3.4. Selected bond lengths (Å) and angles (°) for complex **(3)**

Cl(1)-Au(1)	2.281(2)	Au(1)-P(1)	2.229(2)
Au(1)-Au(2)	3.1669(4)	Au(2)-P(2)	2.245(2)
Au(2)-Cl(2)	2.286(2)	C(4)-C(5)	1.367(12)
C(4)-C(3)	1.379(11)	P(2)-C(21)	1.802(7)
P(2)-C(1)	1.874(7)	P(1)-C(3)	1.808(7)
P(1)-C(1)	1.876(7)	C(2)-N(1)	1.125(11)
<hr/>			
P(1)-Au(1)-Cl(1)	176.84(7)	P(1)-Au(1)-Au(2)	79.88(5)
Cl(1)-Au(1)-Au(2)	103.28(5)	P(2)-Au(2)-Cl(2)	175.21(8)
P(2)-Au(2)-Au(1)	92.01(5)	Cl(2)-Au(2)-Au(1)	92.15(6)
C(21)-P(2)-C(15)	107.9(3)	C(21)-P(2)-C(1)	103.7(3)
C(15)-P(2)-C(1)	104.1(3)	C(21)-P(2)-Au(2)	113.2(3)
C(1)-P(1)-Au(1)	111.9(2)	C(2)-C(1)-H(1)	108.9
N(1)-C(2)-C(1)	179.5(9)		

Complex **3** can be compared to the related [(ClAu)₂dppm] complex which exists in the solid state as two identified polymorphs. The first polymorph (monoclinic) reported in 1977 by Schmidbaur^[9b] contains an intramolecular Au···Au interaction of 3.351(2) Å with no intermolecular Au···Au interaction, whilst the second polymorph (triclinic) obtained through a completely different synthesis route and starting with an Au(III) precursor,^[10] contains neither intra- (5.617(3) Å) nor intermolecular Au···Au interactions.

The cause for the structural difference between the two polymorphs can be found in two different conformational structures for dppm, in which the Au-P···P-Au torsion angles are vastly different at 67.1° (intramolecular present) and 124.3° (intramolecular absent). Of the two polymorphs, complex **3** (orthorhombic) obtained in this study with the Au-P···P-Au torsion angle of 29.20(7)° (intramolecular present), resembles the mentioned monoclinic polymorph more closely in the sense that it also contains an intramolecular interaction, albeit shorter by almost 0.2 Å. The simple substitution of a proton with a CN group on the bridging carbon atom can thus alter the structure considerably.

Complex **3** does not form any polymeric chains or discrete dimers in the crystal lattice due to the lack of intermolecular Au···Au interactions and has the structural pattern of **B** (Fig. 1.13, Chapter 1). The deprotonated form of complex **3** has a remarkable reactivity towards bis(diphenylphosphino)alkane gold(I) complexes (Section 3.2.2.3). The effect of the CN group seems to alter the reactivity of complex **3** considerably compared to the common [(XAu)₂dppm] systems (X= Cl, Br, I, to name a few).

Based on the factors that are now established and considered in the established concept of polymorphism as mentioned in literature (Chapter 1), it might not be surprising that complex **3** also reveals another polymorph in future studies. Initial inroads on the luminescence of dppm-CN based complexes were made by studying the luminescence at room temperature of **3** after excitation. It appeared that the complex is non-emissive at room temperature, and only an emission peak at 402 nm (presumably caused by Schottky defects) for the NMR glass tube that obtained the sample, was obtained. This should be repeated at 77K as well (did not form part of this study).

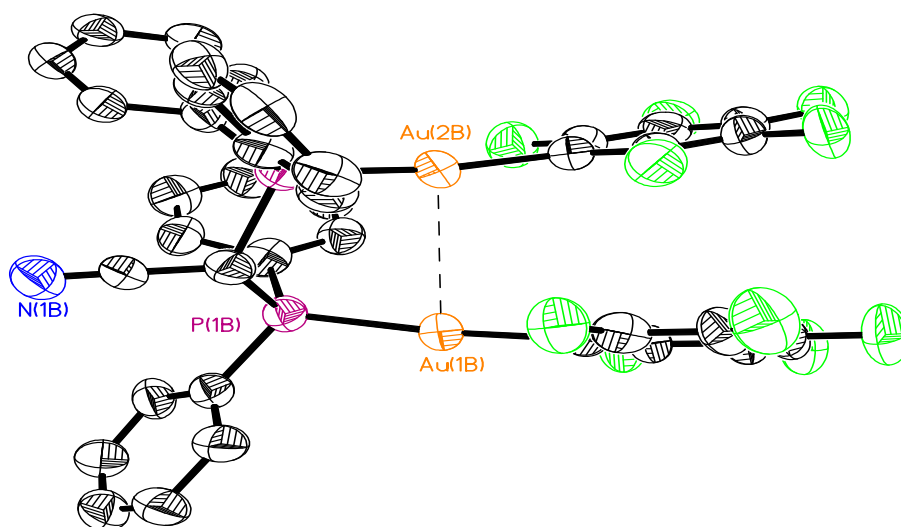
3.2.2.2 The open-ended [(C₆F₅Au)₂(dppm-CN)] Complex (**4**)

The formation of [(C₆F₅Au)₂(dppm-CN)], **4**, was obtained in a manner similar to complex **3**, namely in a DCM solution from the reaction between **2** and [AuC₆F₅(tht)] (mol ratio 1:2) and isolated in high yield (83%). Similar to complex **3** the coordination of the bridging phosphine to Au(I) was evident from the solution ³¹P NMR of **4** that featured a main resonance at δ = +42.0

for two equivalent P atoms. The ^1H NMR C-H resonance at $\delta = 4.71$ ($^2J_{\text{PH}} = 10.85$ Hz, 1H) on the bridging carbon is split into a binomial triplet by a pair of equivalent adjacent ^{31}P nuclei. The IR spectrum depicted a sharp peak at 2137 cm^{-1} assigned to a cyanide stretch. The purity of the product was verified by subjecting complex **4** to elemental analysis and mass spectrometry (M^+ ion peak = 1138), both results were in accord with the expected results.

Complex **4** (triclinic) also forms an open-ended complex and in the crystalline state owing to $\text{Au}\cdots\text{Au}$ interactions, the complex occurs as a dimer (as observed in complex **2**) (Fig. 3.4) in the solid state and contains intramolecular $\text{Au}\cdots\text{Au}$ interactions of $3.0902(7)\text{ \AA}$ for $\text{Au}(1\text{A})\cdots\text{Au}(2\text{A})$ and $3.0809(6)\text{ \AA}$ for $\text{Au}(1\text{B})\cdots\text{Au}(2\text{B})$. The $\text{C}-\text{C}\equiv\text{N}$ moiety is also linear $178.2(18)^\circ$ as observed for complex **3** and the $\text{C}\equiv\text{N}$ bond at $1.100(16)\text{ \AA}$ agrees well with the literature value for the free ligand at $1.148(3)\text{ \AA}$.^[8a] Both the P-Au-C angles are slightly distorted linear with values of $\text{P}(1\text{A})-\text{Au}(1\text{A})-\text{C}(33\text{A}) = 173.2(3)^\circ$ and $\text{P}(1\text{B})-\text{Au}(1\text{B})-\text{C}(33\text{B}) = 174.3(3)^\circ$.

Unlike complex **3** the geometry of the carbon bridging the two P atoms, $\text{P}(1\text{A})-\text{C}(1\text{A})-\text{P}(2\text{A})$ is slightly distorted tetrahedral at $112.2(6)^\circ$, the angle is slightly open to accommodate the configuration of the bulky pentafluorophenyl rings. The $\text{P}-\text{C}_{\text{Ph}}$ bond length is shorter at $1.814(16)\text{ \AA}$ than the $\text{P}-\text{C}$ bond length at $1.874(11)\text{ \AA}$ for the bridging carbon.



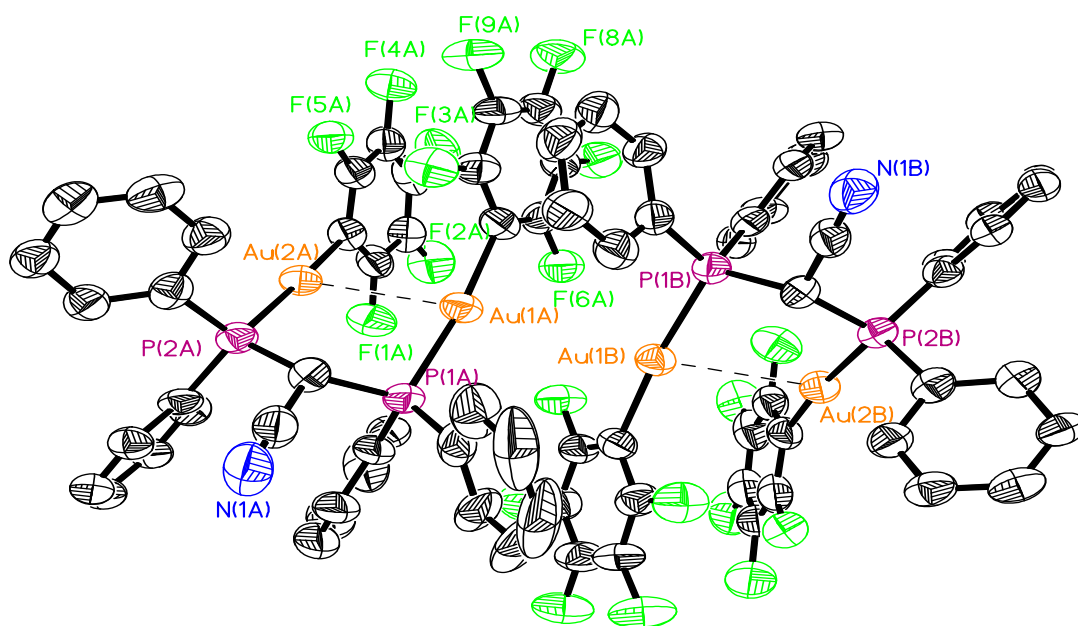


Figure 3.4. Above: Molecular structure of (**4**). The cyano nitrogen atom is in position for further coordination to other metal centres. Below: Showing unique dimer formation. Both structures drawn at 50% probability level and hydrogen atoms are omitted for clarity.

Complex **4** can be compared with the related complex $[(C_6F_5Au)dppm]$ (monoclinic) reported in 1992 by Jones and Thöne.^[11] The complex prepared in a similar synthetic route starting with an Au(I) precursor, contains an intermolecular Au...Au interaction of 3.163(1) Å with no intermolecular Au...Au interaction. The P-Au-C units of the complex in literature are also slightly distorted linear with angles of 176.6(3)° and 175.8(3)°, respectively, presumably caused by slight steric repulsion associated with the C₆F₅ units. The carbon bridging the two P atoms is slightly open and more distorted at a bond angle of 113.4(6)° compared to that of complex **4** at 112.2(6)°.

The most intriguing structural feature of complex **4** is the crystal packing motif. This could be described as a "dimer of dinuclear complexes" along an approximate one-dimensional chain. The complex shows a dimer set with an intramolecular Au...Au interaction of 3.090 Å and

intermolecular Au...Au interactions of 3.529 Å, the latter being at the extreme upper limit of what can still be considered an aurophilic interaction (3.6 Å as proposed by Schmidbaur).^[12] The next set of "dimers" are well over 6 Å away, and this appears to be rare, because typically in such cases the dimers are "face-on", yet in this case it is "side-by-side" and in this study it is described as "dimer type II". The most common type is observed for numerous bridging ligands (incl. dithiophosphates, -phosphonates, -carbamates, etc.) where both the intra- and intermolecular Au...Au interactions are approximately the same distance (~3 Å) apart. See Fig. 3.5 as outlined in section 1.1.6, chapter 1.

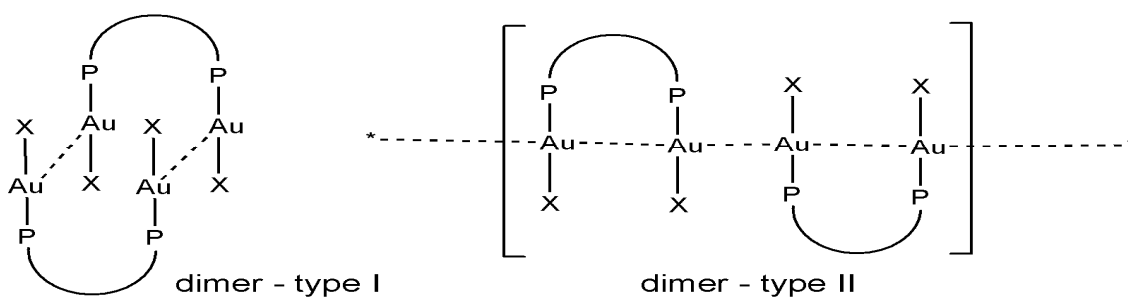


Figure 3.5. The formation of different dimer structures arising from influence of Au...Au interactions between two units. Complex **4** resembles dimer type II.

The dimer arranges itself so that the steric effects from the C₆F₅ units are minimal, and therefore the [(C₆F₅Au)dppm-CN] units arrange in an alternating alignment in the packing (Fig. 3.5, dimer-type II).

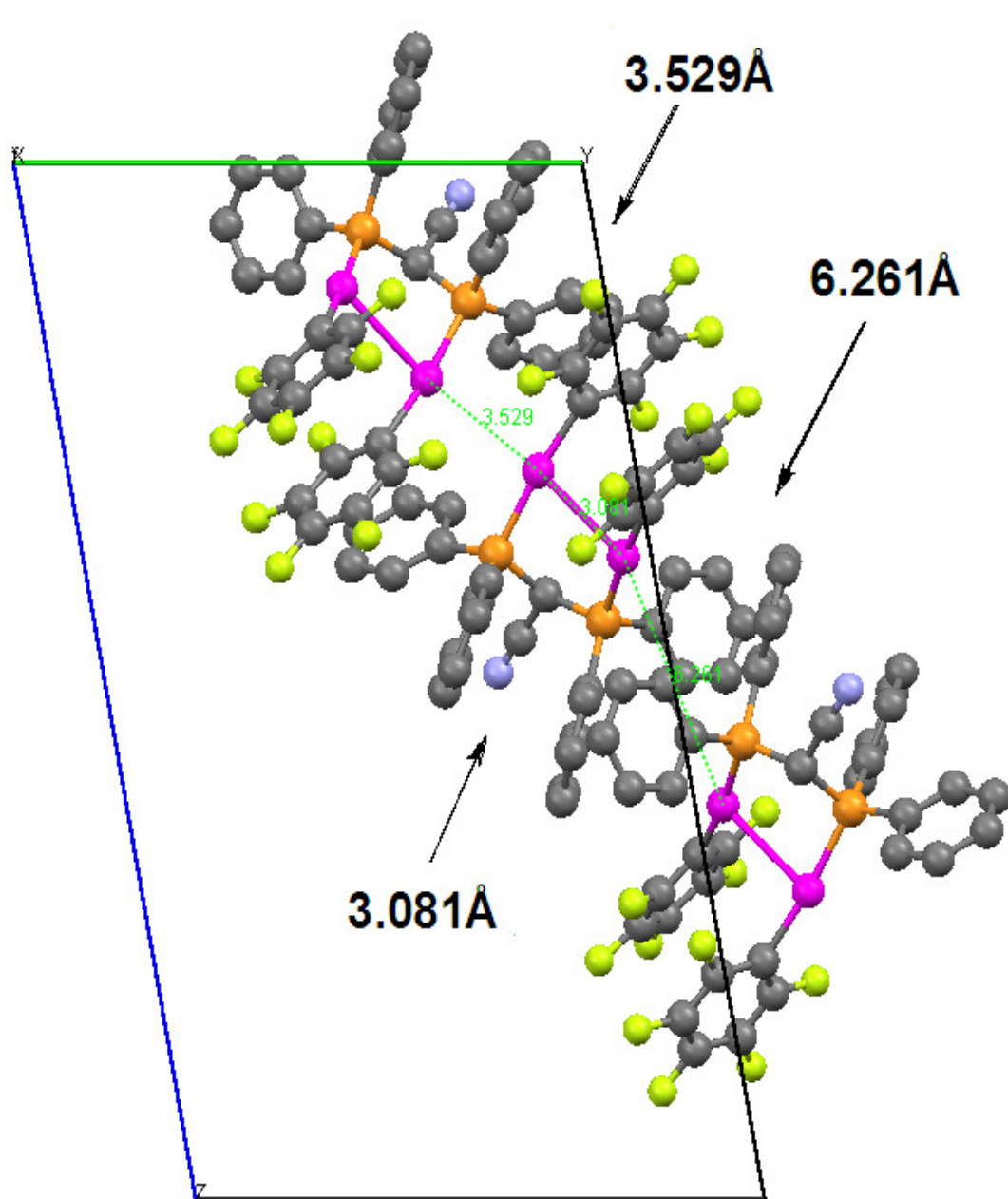


Figure 3.6. A software (Mercury© version: 2.3) generated packing arrangement diagram of the complex (4) as viewed along the a-axis.

Based on these preliminary results and those of related work in literature, complex **4** represent the first example of an open-ended dinuclear gold(I) complex with a structural pattern observed in the dimer-type II. Within the unit cell, the complex **4** has Au...Au separation of 3.090 Å, which is very close to the value of 3.163 Å for the related structure (monoclinic) of [(C₆F₅Au)₂dppm].

One interesting result that can be deduced from this packing arrangement is the observation that the dimer unit of complex **4** (Fig. 3.6) is 6.261 Å away from the other dimer unit. This feature cannot solely be accounted for by intermolecular Au...Au interactions as the driving force since the distance is too far, thus it is presumably simply the packing arrangement driven by hydrogen bonding (H...F). The hydrogen bonding is observed from the alignment between the F atoms of the C₆F₅ units and the phenyl rings of the dppm-CN ligand within the structure. The presence of the CN group appears to have a considerable effect in terms of the structural properties of the gold(I) complexes generated from this ligand, since a similar complex without the CN moiety results in a completely different packing arrangement. The photophysical and photochemical properties of this complex should also be of interest since the emission energy is directly related to the Au...Au separation.

Table 3.5. Crystal data and structure refinement for complex (4)

Empirical formula	$C_{38}H_{21}Au_2F_{10}NP_2$	
Formula weight	1137.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	$a = 10.3567(15)$ Å	$\alpha = 76.668(2)^\circ$.
	$b = 15.125(2)$ Å	$\beta = 80.190(2)^\circ$.
	$c = 24.723(4)$ Å	$\gamma = 70.970(2)^\circ$.
Volume	$3543.4(9)$ Å ³	
Z	4	
Density (calculated)	2.132 Mg/m ³	
Absorption coefficient	8.444 mm ⁻¹	
F(000)	2136	
Crystal size	0.27 x 0.12 x 0.09 mm ³	
Theta range for data collection	1.70 to 25.34°	
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -29 ≤ l ≤ 29	
Reflections collected	51669	
Independent reflections	12896 [R(int) = 0.0688]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5304 and 0.2072	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12896 / 0 / 955	
Goodness-of-fit on F ²	1.219	
Final R indices [I > 2σ(I)]	R1 = 0.0577, wR2 = 0.1770	
R indices (all data)	R1 = 0.0668, wR2 = 0.1849	
Largest diff. peak and hole	4.381 and -1.968 e.Å ⁻³	

Table 3.6. Selected bond lengths (Å) and angles (°) for complex (**4**)

Au(1A)-C(33A)	2.040(10)	Au(1A)-P(1A)	2.271(3)
Au(1A)-Au(2A)	3.0902(7)	Au(2A)-C(27A)	2.057(11)
Au(2A)-P(2A)	2.279(3)	P(1A)-C(21A)	1.814(16)
P(1A)-C(15A)	1.819(14)	P(1A)-C(1A)	1.874(11)
N(1A)-C(2A)	1.100(16)	Au(1B)-C(33B)	2.055(10)
Au(1B)-P(1B)	2.277(3)	Au(1B)-Au(2B)	3.0809(6)
C(33A)-Au(1A)-P(1A)	173.2(3)	C(33A)-Au(1A)-Au(2A)	91.3(3)
C(27A)-Au(2A)-P(2A)	175.0(3)	N(1A)-C(2A)-C(1A)	178.2(18)

3.2.2.3 The neutral cyclic [Au₂{(PPh₂)₂CCN}₂] Complex (**5**)

The neutral dinuclear gold(I) complex [Au₂{(PPh₂)₂CCN}₂], **5**, was prepared in good yield (92%) from the reaction between the anion [(PPh₂)₂CCN]⁻ (obtained from the deprotonation of **2** with ⁿBuLi) and [AuCl(tht)] (mol ratio 1:1). The yield of complex **5** was found to be significantly higher (92%) by prolonged stirring (at least 30 min) when compared with shorter stirring times (<50% yield, 3-5 min stirring) in dichloromethane during the extraction step.

The solution ³¹P NMR spectrum of **5** shows a singlet peak resonating at δ = 42.8 for the P atoms. On the ¹H NMR spectrum there is a disappearance of the proton peak at δ = 3.80 for the free ligand after deprotonation and complexation, only phenyl protons of the eight phenyl rings on the complex remain. An X-ray crystallographic study (Fig. 3.8) of **5** (monoclinic), revealed that it is a cyclic neutral complex. Complex **5** contains Au...Au interactions of 2.8650(4) Å which are in a range of most homobridged dinuclear gold(I) complexes with no intermolecular interactions present in the structure, the short distance suggests complex **5** to be an ideal

candidate for performing oxidative addition reactions with halogens. The C-C≡N moiety is essentially a linear 178.3(5)°, as observed in complexes **3** and **4**, and the C≡N bond at 1.160(7) Å is longer than the corresponding C≡N bond in complexes **3** and **4** and the P-C (central bond distances in **5**) relatively shorter compared to **3** and **4**. This might suggest the delocalisation at the C-C≡N unit and therefore sustaining **5** as a neutral complex (Fig. 3.7)

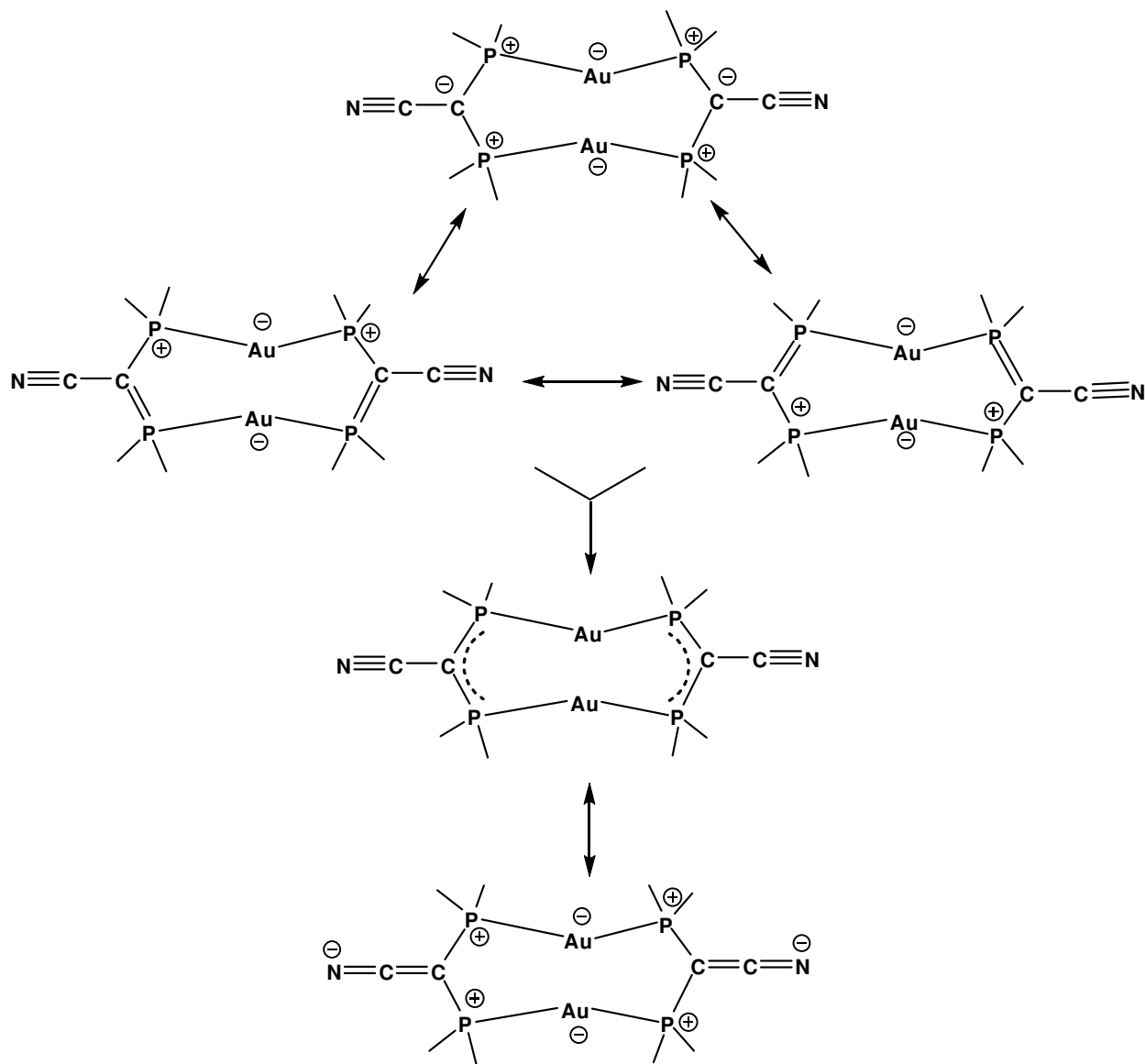


Figure 3.7. Possible resonance structures of complex (**5**) at the C-C≡N unit. Phenyls omitted for clarity

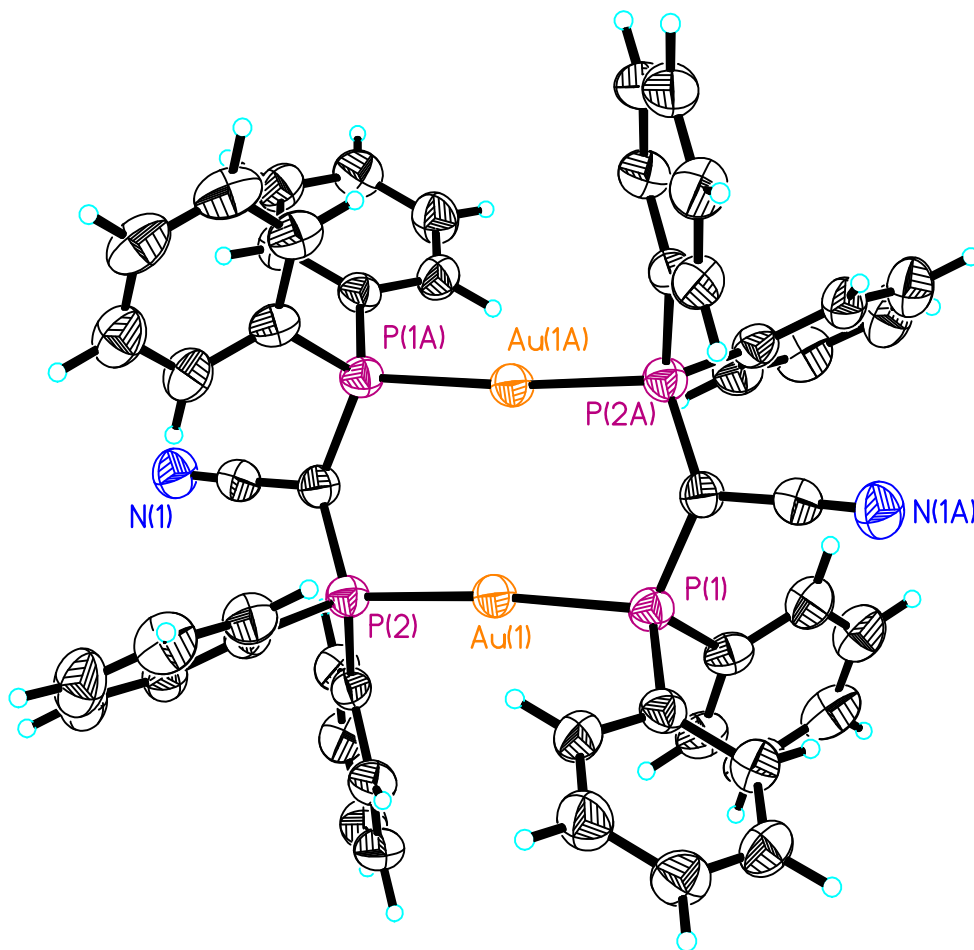


Figure 3.8. Molecular structure of (**5**). Drawing at 50% probability ellipsoids. H atoms shown.

The packing arrangement in the crystal lattice as viewed along the *c*-axis (Fig. 3.9) depict that in complex **5**, there are 2 complete molecules ($Z = 4$) in the asymmetric unit of which the gold(I) centres are quite distant from one another and thus no intermolecular Au...Au interactions are present, the presence of bulky phenyl groups may be responsible for the observed packing arrangement in solid-state.

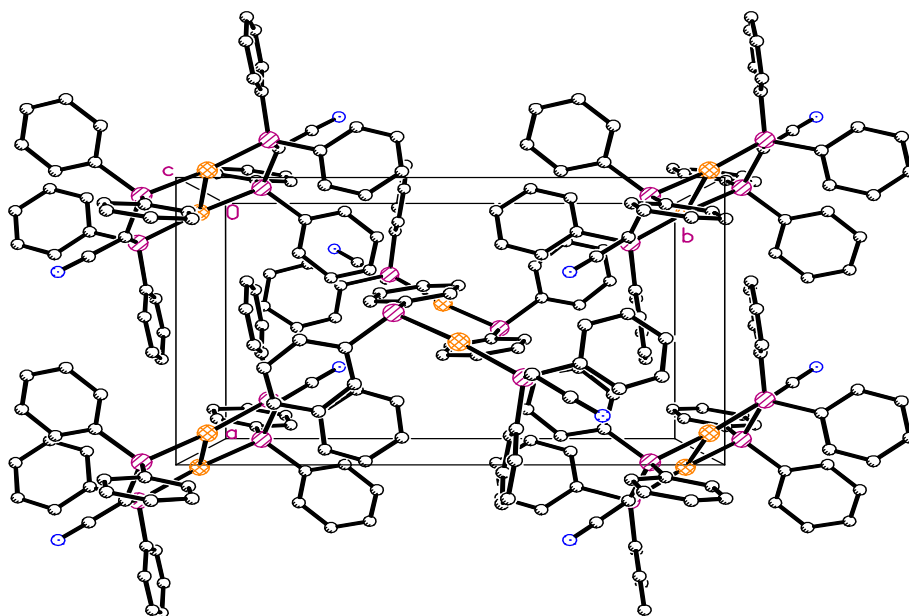


Figure 3.9. Packing arrangement of (**5**) as viewed along the *c*-axis.

Complexes with a Au_2P_4 manifold are mostly *cationic* in nature, and have been reported with a wide variety of anions,^[13] a comparison of complex **5** can be made with a similar complex described by Schmidbaur and Bauer^[14] with the same manifold (Au_2P_4), which has $[\text{Au}(\text{GeCl}_3)_3]^{2-}$ as a dianion. The complex in literature has intramolecular $\text{Au}\cdots\text{Au}$ interactions at 2.97736(4) Å. The P(1)-Au(1)-P(2) unit in complex **5** is less distorted (174.29(4)°) from linearity compared to that reported in literature (172.50(2)°).

Table 3.7. Crystal data and structure refinement for complex (5)

Empirical formula	$C_{52}H_{40}Au_2N_2P_4$	
Formula weight	1210.67	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	$a = 9.6667(6)$ Å	$\alpha = 90^\circ$.
	$b = 14.9403(9)$ Å	$\beta = 90.1420(10)^\circ$.
	$c = 15.3179(9)$ Å	$\gamma = 90^\circ$.
Volume	$2212.3(2)$ Å ³	
Z	2	
Density (calculated)	1.817 Mg/m ³	
Absorption coefficient	6.808 mm ⁻¹	
F(000)	1168	
Crystal size	$0.39 \times 0.28 \times 0.26$ mm ³	
Theta range for data collection	1.90 to 25.36°	
Index ranges	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$	
Reflections collected	31123	
Independent reflections	4058 [R(int) = 0.0664]	
Completeness to theta = 25.36°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2666 and 0.1750	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4058 / 0 / 271	
Goodness-of-fit on F ²	1.098	
Final R indices [I > 2sigma(I)]	R1 = 0.0338, wR2 = 0.0903	
R indices (all data)	R1 = 0.0350, wR2 = 0.0911	
Largest diff. peak and hole	1.771 and -1.889 e.Å ⁻³	

Table 3.8. Selected bond lengths (Å) and angles (°) for complex **(5)**

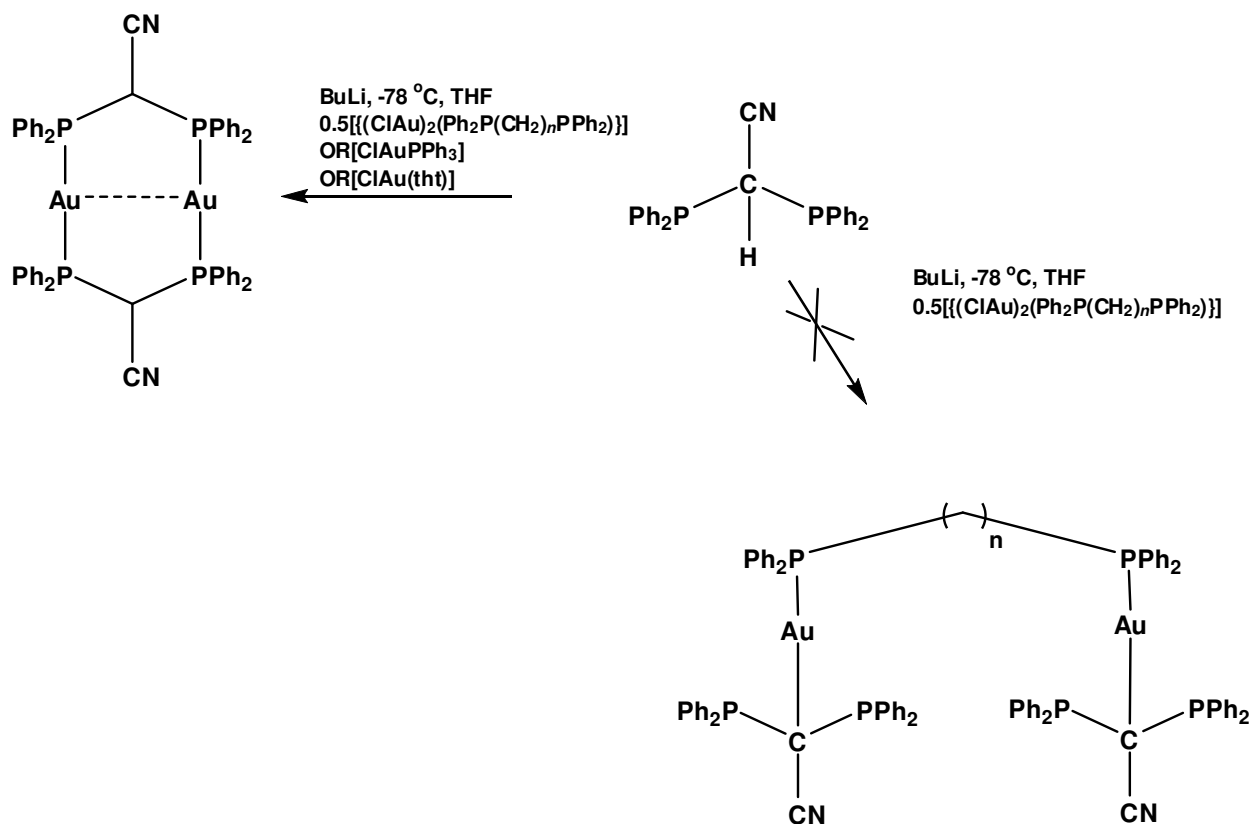
Au(1)-P(1)	2.3146(13)	Au(1)-P(2)	2.3185(13)
Au(1)-Au(1)#1	2.8650(4)	P(1)-C(1)#1	1.762(5)
P(1)-C(21)	1.819(5)	P(1)-C(15)	1.826(5)
P(2)-C(1)	1.759(5)	P(2)-C(3)	1.822(5)
N(1)-C(2)	1.160(7)		
<hr/>			
P(1)-Au(1)-P(2)	174.29(4)	P(1)-Au(1)-Au(1)#1	91.15(3)
P(2)-Au(1)-Au(1)#1	93.13(3)	C(1)#1-P(1)-C(21)	107.9(2)
C(1)#1-P(1)-C(15)	109.1(2)	C(21)-P(1)-C(15)	103.5(2)
N(1)-C(2)-C(1)	178.3(5)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

This study unexpectedly established that complex **5** can also be prepared from the reaction between Li[(PPh₂)₂CCN] and [ClAu(PPh₃)] (mol ratio 1:1) in an initial and reasonable expectation that it may form the organogold(I) complex [(PPh₂)₂C(AuPPh₃)(CN)], especially since, firstly, neutral complexes such as [Au₂{(PPh₂)₂C(H)(C₆F₅Au)}₂] were previously reported by Usón and co-workers,^[15] and secondly Au-C bonds are relatively stable, including those with a negative charge on the C atom.

With the reaction conditions which include reactions between $\text{Li}[(\text{PPh}_2)_2\text{CCN}]$ and $[\text{AuCl}(\text{PPh}_3)]$ there is a formation of complex **5** as main product and as a result eliminate PPh_3 in the process. Furthermore, it was observed that changing from PPh_3 to a series of bis(phosphine) ligands such as $(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$ ($n = 1-6$) (molar ratio 1: 0.5) in the expectation that the latter may introduce more stability through possible $\text{Au}\cdots\text{Au}$ interactions, appeared to make no difference as complex **5** consistently formed as main product (Scheme 3.2)



Scheme 3.2. The reactions of dppm-CN with formation of neutral closed-ended gold(I) complex (**5**). The reaction scheme shows the reaction of gold(I) prefers the making and breaking of Au-P bonds instead of attack on a anionic carbon atom.

Cationic complexes such as $[\text{Au}_2(\text{dppm})_2]^{2+}$ and related systems have been well studied, especially with regard to their structure-photochemistry correlations^[16] and photocatalytic activity.^[17] Such cationic $[\text{Au}_2(\text{dppm})_2]^{2+}$ complexes can also be deprotonated leading to neutral $[\text{Au}_2(\text{Ph}_2\text{P}-\text{CH}-\text{PPh}_2)_2]$ type complexes.^[15]

Of significance in the present study is that the reaction between $[\text{Au}_2\text{Cl}_2(\text{L-L})]$ (L-L = bis(phosphine) ligand such as dppm, dppe, dpph, etc.) and $\text{Li}[(\text{PPh}_2)_2\text{CCN}]$ (molar ratio 1:2), the bis(phosphine) ligand is completely dissociated from the Au centre and replaced by the anionic $[(\text{PPh}_2)_2\text{CCN}]^-$ ligand, thereby facilitating both the cleavage and formation of Au-P bonds, as shown in Scheme 3.2.

This scenario is different compared to the formation of complexes such as $[\text{Au}_2\{(\text{PPh}_2)_2\text{CH}(\text{AuC}_6\text{F}_5)\}_2]$ ^[15] where a *weakly coordinating* ligand (such as tht) can act as leaving group and the metal center can bind to the bridging carbon atom directly (where there is excess electron density). In this study, the anion $[(\text{PPh}_2)_2\text{CCN}]^-$ has no affinity to bind the $[\text{Au-PR}_3]^+$ fragment (which is isolobal to H^+) forming an Au-C bond, but instead replaces a neutral mono- or (bis)phosphine with the stated anion. Presumably the function of CN group is to delocalize the charge more evenly between the P atoms (Fig. 3.7).

This study shows a rare, if not sole example of a dinuclear gold(I) complex with a bridging *neutral* bis(phosphines) to be completely replaced by *anionic* bis(phosphine)s, whilst retaining dinuclearity. Usually the opposite occurs: for example, dinuclear gold(I) dithiophosphate complexes such as $[\text{AuS}_2\text{PR}(\text{OR}')_2]$ readily react with *neutral* bis(phosphines) replacing the ligand $[\text{S}_2\text{PR}(\text{OR}')_2]^-$, which not only contains sulfur as a 'soft' coordinating atom, but is *anionic* as well.^[18] Investigations into the reactivity of complex (**5**) have not been performed in the present study, but those conducted by Usón *et al.*,^[15] and Ruiz *et al.*,^[19] on related systems are a source of inspiration.

In this study complexes of other coinage metal complexes from the dppm-CN ligand such as those of Cu(I) have been performed (Chapter 2, Section 2.8). A dinuclear Cu(I) complex (**6**) was prepared and spectroscopically characterized, the solid state structure of the complex is yet to be confirmed followed by an exploration of the reactivity trends.

3.2.1 Luminescence Studies

To initiate investigations into the luminescence properties of the newly formed gold(I) complexes of the dppm-CN ligand, a study of the $[(\text{ClAu})_2(\text{dppm-CN})]$ complex (**3**) was conducted. This involved excitation of complex **3** under UV at 250 nm at room temperature in the “solid state”. The results from the recorded spectrum depicted that complex **3** is non-emissive at room temperature, with only the emission peak at 402 nm for the NMR glass tube (see Appendix B for the spectrum of the glass tube recorded). The obtained results are not unusual as some dinuclear gold(I) complexes such as $[(\text{Au}(\text{PPh}_3))_2(\text{S}_2\text{C}=\text{C}(\text{CN})_2)]$ was reported non-luminescent at room temperature but brightly luminescent at 77K.^[16]

Qualitatively, a bright blue luminescence of **3** (see Appendix B) was observed when a flask containing **3** was cooled and exposed to a handheld ultraviolet (UV) lamp. Measurements at 77K were not conducted as yet but the observed qualitative results suggest that **3** possesses interesting luminescence properties.

The mononuclear $[\text{AuClPPh}_3]$ complex was found to be luminescent at room temperature in solid state and its emission profile was found to be similar to that of $[\text{BrCuPPh}_3]$, a system which shows that the phosphorescence is similar to PPh_3 and the results suggested that the photoluminescence was an intra-ligand process, perturbed by the bonding of the ligand to the metal atom.^[20]

To obtain a qualitative result as to whether complex **4** is luminescent or not, a flask containing **4** was cooled to 77K and then the sample exposed to a handheld UV lamp, the complex seemed to be a very weak emitter at this temperature (see appendix B), this observed result can presumably be due to the fact that studies^[21] have shown that the effect on the C_6F_5 unit (as contained in **4**) has a quenching effect of the luminescence of complexes with such fluorinated systems.

Further studies to establish the origins of this property and the contribution of the gold(I) centers are essential, as conclusions cannot be drawn based on these qualitative results. The implication of the obtained results for complex **4** are by no means a statement that gold(I) complexes with

the C₆F₅ unit are all non-emissive, as studies involving the use of a heterometallic system [(C₆F₅)₂AuTl(en)]_n showed that the complex has very interesting photoluminescent properties^[22] and a number of perfluoroarylgold complexes have been prepared and their luminescence properties investigated (section 1.1.5, chapter1).

The cyclic gold(I) complex **5** presented in this study is very similar to the previously mentioned complexes.^[16] The luminescence properties of **5** are still to be investigated, although like complexes, **3** and **4** in the solid qualitative results for **5** shows that the complex luminesces at room temperature when exposed to UV light in the solid state. The results from the cationic complexes in literature depict that [Au(dppm)₂][BF₄]₂ has an intense absorption from 220 to 250 nm and this can be attributed to transitions within the phenyl rings, also with an observation that the emission properties are largely influenced by the counterion present.^[16] The change in counterion from BF₄⁻ to Cl⁻ changes the luminescent properties completely, as [Au(dppm)₂]Cl₂ was found to be non-luminescent in solution but luminescent in the solid state. It will, therefore be very interesting to investigate in detail the luminescent properties of complex **5** since it represents a rare example of a gold complex with an Au₂P₄ manifold which is not cationic in nature. Studies involving lifetime measurements and investigation of luminescence properties at 77K for all the gold(I) complexes presented in this study need to be performed.

In summary, in this study a second polymorph of complex (**1**) was isolated, structurally characterized and compared to the polymorphic complex described in literature. New neutral dinuclear gold(I) complexes with the dppm-CN ligand were prepared and characterized, and initial in-roads with an investigation of the luminescence properties and reactivity were made. As shown in this study, the substitution of a proton on the bridging carbon atom with a cyano group can have a significant influence on the chemical reactivity and structure. Further investigations into the reactivity of these complexes are in progress, especially Au-C vs Au-N bond formation for complex (**5**) through variation between precursors [ClAu(PPh₃)] and [C₆F₅Au(tht)], as well as their luminescence properties under UV excitation.

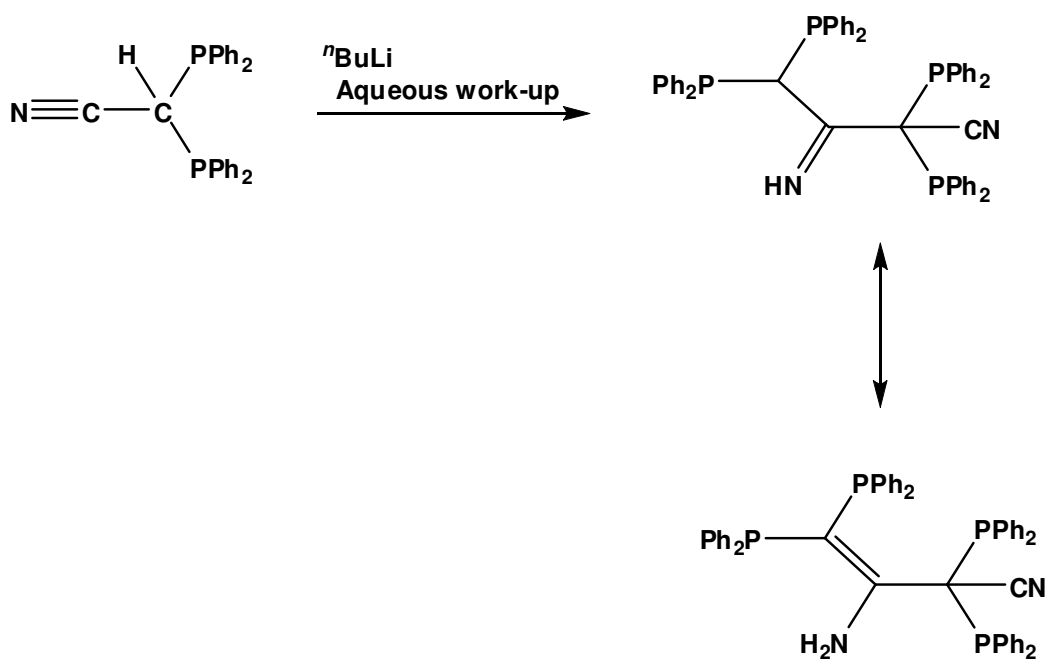
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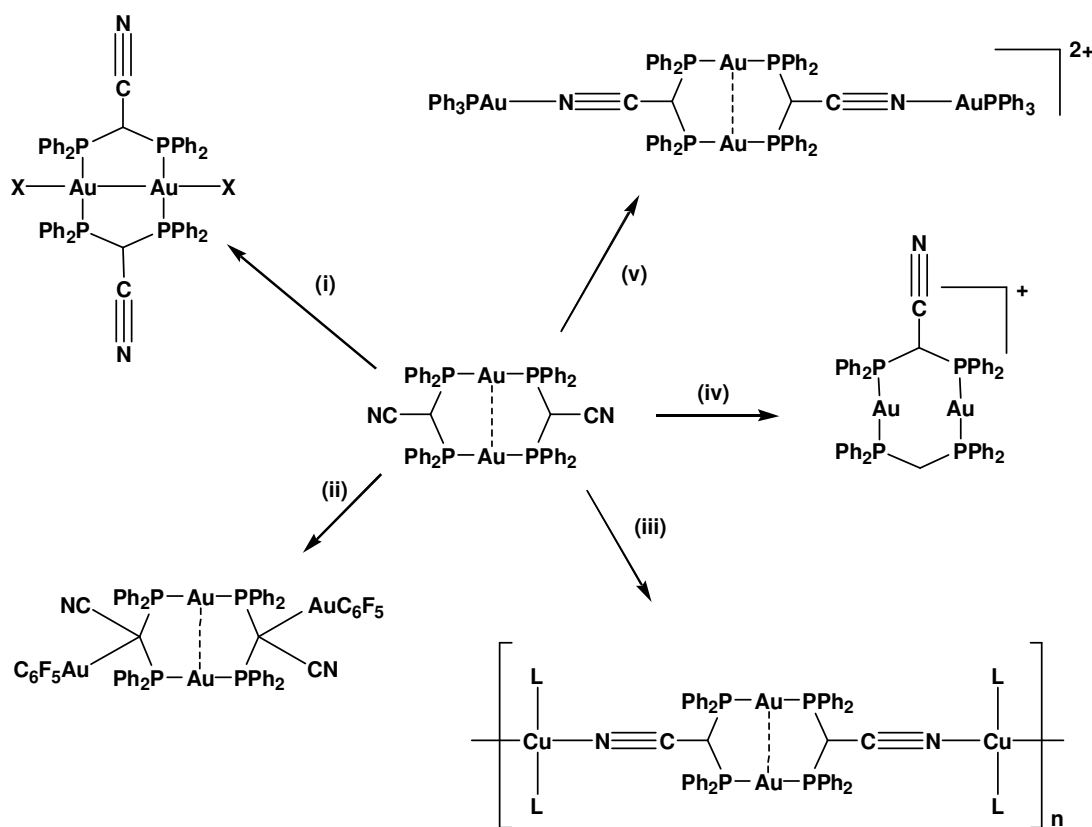
4 Summary and Future Investigations

A second polymorph of $[(ClAu)\{PPh_2(OH)\}]$ has been structurally characterized and compared with the polymorph reported in literature. The dppm-CN ligand has been synthesized using a modified procedure and novel open-ended and closed gold(I) complexes generated. Although there has been development of the ligand by Erker and co-workers (Chapter 1 and 3), there is interest in further developing the ligand by isolation (work in progress) of a novel tetraphosphine (Scheme 4.1) ligand by means of a Thorpe self-condensation reaction for which this system is ideally suited in that the nitrile contains an active α -proton.^[1] Investigation of the luminescence properties of gold(I) complexes and their luminescence properties that may arise from this anticipated multidentate ligand would be of interest.



Scheme 4.1: A potential self-condensation Thorpe reaction of the dppm-CN ligand.

The effect of the cyano group on the newly formed gold(I) complexes bring about interesting properties and there is much interest in developing a series of bi- and heterometallic complexes based on the exploration of the reactivity of the complexes presented in this study (Scheme 4.2.) Performing reactions such as oxidative addition of halogens towards formation of rare Au(II) and (the more abundant) Au(III) complexes is essential, as it has been demonstrated by Nocera and co-workers that Au(III) centers undergo halogen photoreductive elimination reactions and are amongst the ideal class of compounds in the development of catalysts for renewable energy systems.^[2] Whether halogens will preferably attack the cyano nitrogen remains to be seen.



Scheme 4.2. Possible structures of di- and heterometallic complexes that can be generated with addition of (i) X_2 where $X = Cl, Br, I$; (ii) $[AuC_6F_5(tht)]$; (iii) $[Cu(CH_3CN)_4][PF_6]$ with $L = CH_3CN$, (iv) $[Au_2(dppm)_2]^{2+}$ and (v) $[AuClPPh_3]$.

The employment of X-ray crystallography in securing the identities of the complexes in this study is essential, as it assists in the elimination of uncertainty in results that may follow from spectroscopic studies such as NMR and IR.

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Appendix A

The accompanying CD supports this dissertation as an Appendix and has copies of all spectroscopic data, (such as NMR and IR), as well as complete X-ray crystallographic data. Please consult the CD for further information on this data.

Appendix B

Atomic Coordinates

1. Complex [(ClAu)Ph₂P(OH)] (1)

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	9607(1)	4371(1)	2898(1)	21(1)
Au(2)	8874(1)	3848(1)	3786(1)	27(1)
Cl(1)	10067(1)	2670(1)	3613(1)	28(1)
Cl(2)	8931(1)	5974(1)	4251(1)	37(1)
P(1)	9170(1)	6011(1)	2231(1)	23(1)
P(2)	8769(1)	1728(1)	3507(1)	27(1)
O(1)	9059(1)	7154(2)	2765(2)	34(1)
O(2)	9173(1)	976(3)	3237(2)	41(1)
C(1)	8597(1)	5459(4)	1619(2)	24(1)
C(2)	8182(2)	6080(4)	1658(3)	37(1)
C(3)	7748(2)	5670(5)	1175(3)	51(1)
C(4)	7723(2)	4651(5)	657(3)	47(1)
C(5)	8127(2)	4011(5)	630(3)	44(1)
C(6)	8568(2)	4403(4)	1113(3)	35(1)
C(7)	9439(1)	6894(3)	1576(2)	24(1)
C(8)	9561(1)	6238(4)	969(2)	29(1)
C(9)	9780(2)	6877(4)	485(3)	38(1)
C(10)	9883(2)	8194(5)	597(3)	43(1)
C(11)	9760(2)	8859(4)	1187(3)	43(1)
C(12)	9539(1)	8222(4)	1687(3)	33(1)
C(13)	8713(1)	853(4)	4367(2)	27(1)
C(14)	8867(2)	-425(4)	4518(3)	34(1)
C(15)	8812(2)	-1070(4)	5187(3)	42(1)
C(16)	8608(2)	-442(4)	5704(3)	40(1)

C(17)	8456(2)	823(4)	5551(3)	37(1)
C(18)	8508(1)	1480(4)	4900(2)	30(1)
C(19)	8241(1)	1317(4)	2729(2)	27(1)
C(20)	8146(2)	11(4)	2501(3)	36(1)
C(21)	7734(2)	-307(4)	1926(3)	41(1)
C(22)	7407(2)	648(4)	1570(3)	39(1)
C(23)	7504(2)	1929(4)	1789(3)	43(1)
C(24)	7921(2)	2261(4)	2357(3)	38(1)

Table 2. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	20(1)	22(1)	21(1)	3(1)	5(1)	2(1)
Au(2)	27(1)	23(1)	33(1)	-4(1)	12(1)	-2(1)
Cl(1)	24(1)	28(1)	32(1)	8(1)	6(1)	5(1)
Cl(2)	52(1)	27(1)	37(1)	-8(1)	22(1)	-5(1)
P(1)	24(1)	21(1)	22(1)	2(1)	4(1)	4(1)
P(2)	23(1)	24(1)	35(1)	-4(1)	11(1)	-1(1)
O(1)	47(2)	26(1)	30(2)	0(1)	12(2)	7(1)
O(2)	31(2)	31(2)	67(2)	-13(2)	24(2)	-1(1)
C(1)	21(2)	29(2)	21(2)	6(2)	5(2)	0(2)
C(2)	23(2)	38(2)	50(3)	-2(2)	11(2)	5(2)
C(3)	23(3)	57(3)	72(4)	0(3)	14(3)	9(2)
C(4)	23(3)	61(3)	49(3)	9(2)	-4(2)	-4(2)
C(5)	35(3)	53(3)	37(3)	-5(2)	0(2)	-4(2)
C(6)	23(2)	42(2)	39(3)	-10(2)	8(2)	2(2)
C(7)	17(2)	27(2)	24(2)	6(2)	-3(2)	2(2)
C(8)	26(2)	31(2)	28(2)	6(2)	5(2)	3(2)
C(9)	33(3)	52(3)	26(2)	13(2)	3(2)	1(2)
C(10)	25(3)	57(3)	43(3)	21(2)	4(2)	-7(2)
C(11)	33(3)	35(2)	52(3)	9(2)	-5(2)	-13(2)
C(12)	27(2)	28(2)	38(3)	4(2)	0(2)	-2(2)
C(13)	21(2)	25(2)	30(2)	-4(2)	0(2)	-5(2)
C(14)	32(3)	31(2)	36(3)	-7(2)	3(2)	0(2)
C(15)	53(3)	25(2)	40(3)	4(2)	-2(2)	-2(2)
C(16)	52(3)	35(2)	29(3)	1(2)	3(2)	-10(2)
C(17)	44(3)	35(2)	32(3)	-5(2)	12(2)	-6(2)
C(18)	29(2)	26(2)	33(2)	-1(2)	5(2)	0(2)
C(19)	31(2)	28(2)	28(2)	0(2)	16(2)	-2(2)
C(20)	36(3)	28(2)	41(3)	-2(2)	7(2)	0(2)
C(21)	43(3)	39(2)	40(3)	-10(2)	12(2)	-9(2)
C(22)	29(3)	59(3)	29(2)	-2(2)	6(2)	-12(2)
C(23)	35(3)	48(3)	41(3)	7(2)	3(2)	7(2)

C(24)

40(3)

31(2)

42(3)

1(2)

11(2)

0(2)

Table 3. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1)	9059	6853	3210	51
H(2)	9435	1363	3419	62
H(2B)	8198	6785	2016	45
H(3)	7465	6095	1201	61
H(4)	7423	4389	316	56
H(5)	8107	3294	278	52
H(6)	8849	3951	1096	42
H(8)	9491	5334	889	34
H(9)	9862	6416	73	45
H(10)	10038	8638	265	51
H(11)	9827	9767	1256	52
H(12)	9457	8687	2097	40
H(14)	9010	-863	4167	41
H(15)	8916	-1950	5287	51
H(16)	8574	-881	6161	49
H(17)	8311	1253	5902	44
H(18)	8405	2361	4810	36
H(20)	8365	-655	2744	43
H(21)	7673	-1193	1769	49
H(22)	7120	419	1180	47
H(23)	7283	2592	1549	52
H(24)	7987	3154	2493	45

2. Complex [(ClAu)₂(dppm-CN)] (3)

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	-762(2)	8257(2)	9224(1)	56(1)
Au(1)	-592(1)	8669(1)	7732(1)	48(1)
Au(2)	1484(1)	7808(1)	7256(1)	51(1)
C(4)	-452(5)	8105(7)	4587(5)	50(2)
Cl(2)	1355(2)	6467(2)	8282(2)	69(1)
P(2)	1692(1)	9036(2)	6181(1)	44(1)
P(1)	-510(1)	9107(2)	6275(1)	44(1)
C(5)	-428(6)	7239(8)	4036(6)	63(2)
C(6)	-414(6)	6240(7)	4409(6)	57(2)
C(7)	-388(5)	6106(6)	5327(6)	51(2)
C(8)	-406(5)	6990(6)	5898(6)	50(2)
C(3)	-442(5)	7994(5)	5514(5)	41(1)
C(15)	2655(5)	9971(6)	6416(5)	49(2)
C(16)	3248(5)	9752(7)	7136(5)	54(2)
C(17)	4056(6)	10377(7)	7298(7)	70(2)
C(19)	3635(6)	11447(7)	6058(8)	68(3)
C(20)	2838(5)	10835(6)	5887(6)	57(2)
C(1)	603(5)	9886(5)	6014(5)	45(2)
C(9)	-1500(5)	9924(6)	5901(5)	48(2)
C(10)	-1467(5)	10590(7)	5165(6)	58(2)
C(11)	-2286(6)	11138(6)	4897(7)	65(2)
C(14)	-2361(5)	9810(5)	6381(5)	50(2)
C(2)	620(5)	10809(7)	6594(6)	57(2)
N(1)	639(6)	11521(7)	7045(7)	86(3)
C(21)	1903(5)	8482(6)	5076(5)	44(2)
C(22)	1955(6)	9097(6)	4297(5)	54(2)
C(23)	2103(6)	8614(8)	3471(6)	64(2)

C(25)	2138(6)	6929(7)	4167(6)	54(2)
C(26)	1985(5)	7393(5)	4999(5)	48(2)
C(18)	4224(6)	11235(7)	6765(8)	70(3)
C(24)	2203(6)	7542(7)	3403(6)	58(2)
C(13)	-3161(6)	10369(7)	6115(6)	59(2)
C(12)	-3136(6)	11007(7)	5390(7)	67(2)

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	63(1)	55(1)	52(1)	0(1)	6(1)	2(1)
Au(1)	49(1)	53(1)	44(1)	-1(1)	3(1)	2(1)
Au(2)	52(1)	54(1)	46(1)	2(1)	-2(1)	4(1)
C(4)	41(4)	59(4)	50(4)	2(3)	3(3)	6(3)
Cl(2)	77(1)	70(1)	58(1)	12(1)	4(1)	8(1)
P(2)	41(1)	46(1)	44(1)	-4(1)	-4(1)	2(1)
P(1)	39(1)	49(1)	45(1)	-1(1)	-2(1)	3(1)
C(5)	56(5)	93(7)	41(4)	-6(4)	2(4)	4(4)
C(6)	46(4)	63(5)	63(5)	-20(4)	9(4)	-9(4)
C(7)	49(4)	48(4)	56(5)	-9(3)	9(4)	-7(3)
C(8)	49(4)	47(4)	55(4)	-3(3)	4(3)	-14(3)
C(3)	34(3)	47(4)	41(4)	1(3)	-4(3)	-2(3)
C(15)	40(3)	52(4)	55(4)	-16(3)	-6(3)	5(3)
C(16)	45(4)	71(5)	46(4)	-16(4)	1(3)	3(3)
C(17)	59(4)	84(6)	66(5)	-19(5)	-18(5)	2(4)
C(19)	55(5)	44(4)	106(8)	-5(4)	-3(5)	-2(3)
C(20)	47(4)	46(4)	78(5)	-5(4)	-8(4)	1(3)
C(1)	44(4)	45(4)	46(4)	-7(3)	-5(3)	5(3)
C(9)	43(4)	47(4)	54(4)	-5(3)	-2(3)	8(3)
C(10)	46(4)	61(5)	66(5)	12(4)	-2(4)	-1(3)
C(11)	63(5)	50(5)	82(6)	12(4)	-21(5)	-1(4)
C(14)	51(4)	40(4)	58(4)	-7(3)	1(3)	-2(3)
C(2)	42(4)	63(5)	67(5)	-17(4)	-8(4)	5(3)
N(1)	72(5)	71(5)	115(8)	-45(5)	-15(5)	14(4)
C(21)	33(3)	52(4)	48(4)	-6(3)	-4(3)	-1(3)
C(22)	63(5)	45(4)	52(4)	1(3)	5(4)	0(4)
C(23)	66(5)	76(6)	51(5)	7(4)	7(4)	2(4)
C(25)	49(4)	53(4)	61(5)	-12(4)	-3(4)	1(3)
C(26)	43(4)	45(4)	55(4)	3(3)	-7(3)	-1(3)
C(18)	52(5)	59(5)	100(7)	-31(5)	2(5)	-2(4)
C(24)	51(4)	72(5)	51(5)	-6(4)	5(4)	-4(4)

C(13)	46(4)	62(5)	71(5)	-3(4)	-3(4)	0(4)
C(12)	53(5)	66(5)	82(6)	-4(5)	-14(5)	11(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**.

	x	y	z	U(eq)
H(4)	-476	8790	4328	60
H(5)	-420	7325	3398	76
H(6)	-424	5640	4025	69
H(7)	-357	5417	5577	61
H(8)	-394	6905	6536	60
H(16)	3108	9175	7523	65
H(17)	4486	10205	7775	83
H(19)	3775	12027	5674	82
H(20)	2416	11012	5405	69
H(1)	579	10120	5370	54
H(10)	-883	10675	4839	69
H(11)	-2268	11594	4388	78
H(14)	-2393	9350	6887	59
H(22)	1890	9842	4333	64
H(23)	2137	9033	2940	77
H(25)	2198	6185	4122	65
H(26)	1935	6964	5523	57
H(18)	4754	11684	6890	85
H(24)	2317	7224	2832	69
H(13)	-3741	10303	6450	71
H(12)	-3701	11372	5211	80

3. Complex [(C₆F₅Au)₂(dppm-CN)] (4)

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1A)	8840(1)	6597(1)	2083(1)	52(1)
Au(2A)	9020(1)	5386(1)	1207(1)	51(1)
P(1A)	9580(3)	7569(2)	1336(1)	54(1)
P(2A)	10705(3)	5930(2)	655(1)	48(1)
F(1A)	5739(8)	6244(5)	1265(3)	75(2)
F(2A)	3706(8)	5625(7)	1877(4)	86(2)
F(3A)	4262(10)	3904(7)	2563(3)	88(3)
F(4A)	6918(10)	2838(5)	2685(3)	84(2)
F(5A)	8980(8)	3467(5)	2106(3)	63(2)
F(6A)	5990(8)	6472(5)	2816(3)	68(2)
F(7A)	5356(8)	5061(5)	3596(3)	79(2)
F(8A)	7339(9)	3418(5)	3908(3)	82(2)
F(9A)	9938(9)	3162(5)	3427(3)	82(2)
F(10A)	10604(7)	4572(5)	2651(3)	70(2)
N(1A)	12595(16)	7749(10)	312(6)	100(5)
C(1A)	11134(11)	6801(8)	973(5)	50(2)
C(2A)	11982(15)	7332(10)	600(6)	70(3)
C(3A)	12353(12)	5026(8)	600(5)	56(3)
C(4A)	12868(14)	4501(9)	1107(5)	64(3)
C(5A)	14088(15)	3779(9)	1085(6)	72(4)
C(6A)	14790(14)	3549(9)	599(6)	71(3)
C(7A)	14293(13)	4047(8)	94(6)	65(3)
C(8A)	13052(13)	4805(8)	93(5)	59(3)
C(9A)	10253(12)	6521(7)	-46(5)	51(2)
C(10A)	11160(12)	6858(8)	-461(5)	54(3)
C(11A)	10689(16)	7297(8)	-978(5)	67(3)
C(12A)	9391(15)	7414(9)	-1086(5)	65(3)

C(13A)	8510(14)	7089(8)	-669(5)	61(3)
C(14A)	8919(12)	6647(8)	-153(5)	55(3)
C(15A)	10296(17)	8420(10)	1493(6)	76(4)
C(16A)	11390(20)	8042(14)	1820(7)	101(6)
C(17A)	12000(30)	8680(20)	1923(9)	154(12)
C(18A)	11470(40)	9670(30)	1721(14)	190(20)
C(19A)	10440(40)	9973(19)	1421(13)	169(17)
C(20A)	9770(20)	9396(11)	1289(7)	126(9)
C(21A)	8379(18)	8151(9)	815(5)	77(4)
C(22A)	8720(20)	8760(9)	326(6)	94(6)
C(23A)	7710(30)	9173(12)	-54(7)	125(10)
C(24A)	6510(20)	8964(14)	41(8)	110(7)
C(25A)	6184(19)	8394(14)	514(7)	109(7)
C(26A)	7105(16)	7996(9)	905(6)	74(4)
C(27A)	7445(12)	4884(8)	1643(4)	51(2)
C(28A)	7688(13)	4021(8)	2022(5)	55(3)
C(29A)	6636(15)	3684(9)	2329(5)	62(3)
C(30A)	5293(16)	4214(11)	2273(5)	70(4)
C(31A)	5004(13)	5101(9)	1919(5)	60(3)
C(32A)	6091(14)	5386(9)	1613(4)	60(3)
C(33A)	8338(12)	5593(8)	2715(4)	52(3)
C(34A)	7014(12)	5680(8)	2960(5)	52(3)
C(35A)	6670(13)	4966(8)	3362(5)	57(3)
C(36A)	7662(14)	4122(8)	3523(5)	59(3)
C(37A)	8985(13)	4006(8)	3277(5)	56(3)
C(38A)	9278(13)	4742(8)	2877(5)	56(3)
Au(1B)	7506(1)	8280(1)	2971(1)	51(1)
Au(2B)	5628(1)	9507(1)	3802(1)	52(1)
P(1B)	8265(3)	7281(2)	3770(1)	49(1)
P(2B)	7248(3)	8962(2)	4416(1)	46(1)
F(1B)	7943(8)	10303(6)	2446(3)	78(2)
F(2B)	6773(11)	11710(6)	1633(4)	97(3)
F(3B)	4984(10)	11463(6)	1034(3)	93(3)
F(4B)	4325(9)	9813(6)	1275(3)	84(2)
F(5B)	5425(8)	8429(5)	2100(3)	69(2)
F(6B)	4736(9)	11402(5)	2849(3)	77(2)
F(7B)	2509(11)	12162(6)	2299(3)	97(3)

F(8B)	555(10)	11248(7)	2460(4)	98(3)
F(9B)	924(9)	9546(7)	3147(3)	87(2)
F(10B)	3086(8)	8787(6)	3734(3)	79(2)
N(1B)	10373(12)	6945(8)	4923(5)	76(3)
C(1B)	8764(12)	8017(7)	4167(4)	50(2)
C(2B)	9660(12)	7437(8)	4586(5)	56(3)
C(3B)	9848(12)	6336(8)	3698(4)	54(3)
C(4B)	9984(13)	5389(8)	3966(5)	59(3)
C(5B)	11247(15)	4708(10)	3883(5)	71(3)
C(6B)	12295(16)	4950(10)	3554(6)	77(4)
C(7B)	12182(15)	5891(10)	3278(5)	75(4)
C(8B)	10889(15)	6592(10)	3343(5)	74(4)
C(9B)	6977(13)	6819(7)	4228(5)	54(3)
C(10B)	7188(14)	6252(8)	4767(5)	59(3)
C(11B)	6165(16)	5952(8)	5094(6)	67(3)
C(12B)	4933(16)	6180(9)	4898(6)	73(4)
C(13B)	4686(16)	6712(8)	4376(5)	68(3)
C(14B)	5683(12)	7026(8)	4042(5)	55(3)
C(15B)	6609(11)	8459(7)	5107(5)	50(2)
C(16B)	7422(11)	8114(7)	5561(4)	47(2)
C(17B)	6868(12)	7736(8)	6074(5)	55(3)
C(18B)	5561(13)	7672(8)	6148(5)	57(3)
C(19B)	4754(12)	7978(8)	5697(5)	57(3)
C(20B)	5332(12)	8383(7)	5180(5)	51(2)
C(21B)	7997(11)	9867(8)	4469(5)	52(2)
C(22B)	7967(10)	10156(8)	4965(5)	50(2)
C(23B)	8437(12)	10934(7)	4952(5)	57(3)
C(24B)	8946(12)	11404(8)	4446(6)	61(3)
C(25B)	8974(13)	11104(8)	3963(5)	60(3)
C(26B)	8474(13)	10360(8)	3964(5)	59(3)
C(27B)	4027(12)	10080(8)	3328(4)	56(3)
C(28B)	3788(14)	10917(9)	2946(5)	65(3)
C(29B)	2640(17)	11324(9)	2651(5)	72(4)
C(30B)	1674(14)	10867(11)	2726(5)	71(4)
C(31B)	1859(13)	10000(11)	3092(5)	69(3)
C(32B)	2984(13)	9629(9)	3379(5)	59(3)
C(33B)	6747(11)	9287(8)	2295(4)	51(3)

C(34B)	7059(13)	10134(8)	2160(5)	58(3)
C(35B)	6503(13)	10875(8)	1741(5)	61(3)
C(36B)	5588(14)	10765(9)	1443(5)	70(3)
C(37B)	5243(13)	9915(9)	1563(5)	65(3)
C(38B)	5835(12)	9213(8)	1988(4)	52(3)

Table 7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Au(1A)	58(1)	49(1)	48(1)	-1(1)	-5(1)	-22(1)
Au(2A)	54(1)	47(1)	54(1)	-3(1)	-4(1)	-22(1)
P(1A)	64(2)	41(1)	54(2)	-5(1)	4(1)	-19(1)
P(2A)	48(2)	43(1)	55(2)	-7(1)	-4(1)	-17(1)
F(1A)	70(5)	75(5)	70(4)	7(4)	-17(4)	-19(4)
F(2A)	57(5)	108(6)	96(6)	-26(5)	-5(4)	-23(4)
F(3A)	89(6)	112(7)	73(5)	-16(4)	18(4)	-57(5)
F(4A)	109(7)	66(5)	74(4)	8(4)	4(4)	-43(5)
F(5A)	68(5)	53(4)	65(4)	-4(3)	-8(3)	-18(3)
F(6A)	70(5)	57(4)	69(4)	-5(3)	1(3)	-16(3)
F(7A)	65(5)	71(5)	90(5)	-8(4)	14(4)	-23(4)
F(8A)	96(6)	64(4)	83(5)	9(4)	5(4)	-44(4)
F(9A)	77(5)	54(4)	99(6)	14(4)	-18(4)	-14(4)
F(10A)	46(4)	78(5)	79(4)	-4(4)	-8(3)	-18(3)
N(1A)	107(11)	109(10)	109(10)	-53(8)	49(9)	-75(9)
C(1A)	44(6)	49(6)	58(6)	-13(5)	-2(5)	-16(5)
C(2A)	73(9)	70(8)	70(8)	-24(7)	7(7)	-26(7)
C(3A)	56(7)	53(6)	67(7)	-19(5)	-3(5)	-23(5)
C(4A)	65(8)	58(7)	68(7)	-13(6)	-15(6)	-10(6)
C(5A)	79(9)	51(7)	90(9)	-10(6)	-27(8)	-18(6)
C(6A)	57(7)	62(8)	100(10)	-24(7)	-6(7)	-21(6)
C(7A)	60(7)	54(7)	79(8)	-14(6)	4(6)	-20(6)
C(8A)	56(7)	56(7)	65(7)	-8(5)	2(5)	-21(6)
C(9A)	54(6)	32(5)	64(6)	1(4)	-2(5)	-19(4)
C(10A)	48(6)	52(6)	61(6)	-3(5)	-5(5)	-17(5)
C(11A)	88(10)	48(7)	60(7)	-4(5)	7(7)	-25(6)
C(12A)	69(8)	53(7)	66(7)	1(6)	-14(6)	-13(6)
C(13A)	73(8)	46(6)	58(7)	-3(5)	-11(6)	-15(6)
C(14A)	42(6)	57(7)	60(6)	-6(5)	-14(5)	-7(5)
C(15A)	91(11)	82(9)	70(8)	-38(7)	37(8)	-50(8)

C(16A)	126(16)	122(14)	95(11)	-51(11)	20(11)	-83(13)
C(17A)	150(20)	260(30)	122(17)	-130(20)	51(15)	-120(20)
C(18A)	270(50)	230(40)	180(30)	-170(30)	150(30)	-210(40)
C(19A)	240(40)	105(17)	210(30)	-110(20)	130(30)	-130(20)
C(20A)	190(20)	67(10)	128(14)	-53(10)	99(15)	-79(12)
C(21A)	106(12)	47(7)	47(7)	5(5)	4(7)	4(7)
C(22A)	119(13)	52(8)	68(9)	7(6)	19(9)	4(8)
C(23A)	190(20)	65(10)	62(10)	6(7)	12(13)	23(13)
C(24A)	114(16)	97(13)	74(11)	-6(9)	-22(11)	29(12)
C(25A)	77(11)	138(16)	81(11)	-34(11)	-22(9)	25(11)
C(26A)	75(9)	52(7)	65(8)	-2(6)	-2(7)	11(6)
C(27A)	51(6)	58(6)	51(6)	-11(5)	-4(5)	-24(5)
C(28A)	63(7)	57(7)	52(6)	-9(5)	-4(5)	-32(6)
C(29A)	77(9)	61(7)	57(7)	-15(6)	10(6)	-40(7)
C(30A)	87(10)	96(10)	48(6)	-22(6)	8(6)	-57(9)
C(31A)	54(7)	70(8)	63(7)	-22(6)	0(5)	-25(6)
C(32A)	70(8)	67(7)	43(6)	-9(5)	-7(5)	-21(6)
C(33A)	61(7)	57(6)	45(5)	-5(5)	-8(5)	-28(5)
C(34A)	58(7)	48(6)	54(6)	-14(5)	0(5)	-23(5)
C(35A)	63(7)	55(7)	51(6)	-6(5)	4(5)	-22(6)
C(36A)	68(8)	57(7)	57(6)	-4(5)	-8(6)	-28(6)
C(37A)	60(7)	41(6)	66(7)	3(5)	-25(6)	-13(5)
C(38A)	57(7)	52(6)	61(7)	-2(5)	-13(5)	-21(5)
Au(1B)	50(1)	50(1)	47(1)	-5(1)	-9(1)	-8(1)
Au(2B)	47(1)	50(1)	53(1)	-8(1)	-11(1)	-4(1)
P(1B)	53(2)	44(1)	47(1)	-9(1)	-10(1)	-8(1)
P(2B)	45(1)	39(1)	51(1)	-8(1)	-4(1)	-11(1)
F(1B)	75(5)	77(5)	88(5)	-7(4)	-22(4)	-30(4)
F(2B)	106(7)	60(5)	124(7)	15(4)	-19(6)	-43(5)
F(3B)	102(7)	67(5)	92(5)	28(4)	-34(5)	-20(5)
F(4B)	82(6)	88(6)	83(5)	8(4)	-39(4)	-28(4)
F(5B)	80(5)	54(4)	76(4)	7(3)	-27(4)	-29(4)
F(6B)	95(6)	62(4)	71(5)	-13(4)	-8(4)	-19(4)
F(7B)	114(7)	68(5)	85(5)	0(4)	-42(5)	13(5)
F(8B)	93(6)	101(6)	84(5)	-24(5)	-45(5)	14(5)
F(9B)	61(5)	113(7)	84(5)	-24(5)	-12(4)	-16(5)
F(10B)	66(5)	91(5)	74(5)	0(4)	-11(4)	-22(4)

N(1B)	70(7)	71(7)	82(7)	-28(6)	-23(6)	4(6)
C(1B)	53(6)	41(5)	51(6)	-12(4)	-3(5)	-6(5)
C(2B)	46(6)	60(7)	53(6)	-19(5)	-7(5)	4(5)
C(3B)	59(7)	52(6)	46(6)	-13(5)	-11(5)	-2(5)
C(4B)	65(8)	48(6)	61(7)	-14(5)	-24(6)	-3(5)
C(5B)	73(9)	68(8)	65(7)	-24(6)	-8(7)	-2(7)
C(6B)	77(10)	71(9)	71(8)	-29(7)	-23(7)	13(7)
C(7B)	64(8)	68(8)	69(8)	-11(6)	3(6)	4(6)
C(8B)	75(9)	69(8)	58(7)	-14(6)	1(6)	3(7)
C(9B)	76(8)	38(5)	54(6)	-10(5)	-10(5)	-22(5)
C(10B)	82(9)	42(6)	53(6)	-9(5)	-17(6)	-13(6)
C(11B)	87(10)	42(6)	68(8)	0(5)	-7(7)	-20(6)
C(12B)	77(10)	60(8)	80(9)	-8(6)	-6(7)	-21(7)
C(13B)	85(9)	44(6)	77(8)	4(6)	-12(7)	-29(6)
C(14B)	58(7)	55(6)	54(6)	-13(5)	-10(5)	-19(5)
C(15B)	48(6)	42(5)	57(6)	-10(5)	-12(5)	-4(5)
C(16B)	44(6)	41(5)	54(6)	-9(4)	-4(4)	-12(4)
C(17B)	51(7)	49(6)	54(6)	-9(5)	-9(5)	-1(5)
C(18B)	64(8)	40(6)	55(6)	-11(5)	1(5)	0(5)
C(19B)	48(6)	47(6)	75(8)	-16(5)	2(5)	-15(5)
C(20B)	53(6)	38(5)	59(6)	-5(5)	-4(5)	-13(5)
C(21B)	43(6)	48(6)	64(6)	-15(5)	4(5)	-13(5)
C(22B)	33(5)	54(6)	59(6)	-12(5)	-3(4)	-8(4)
C(23B)	60(7)	37(5)	74(7)	-7(5)	-19(6)	-12(5)
C(24B)	49(7)	44(6)	91(9)	-6(6)	-14(6)	-16(5)
C(25B)	54(7)	47(6)	74(8)	-8(5)	7(6)	-15(5)
C(26B)	65(7)	47(6)	62(7)	-11(5)	0(6)	-13(5)
C(27B)	58(7)	54(6)	43(5)	-10(5)	-3(5)	-1(5)
C(28B)	64(8)	71(8)	50(6)	-22(6)	-13(6)	5(6)
C(29B)	90(10)	53(7)	53(7)	-7(5)	-16(7)	7(7)
C(30B)	61(8)	80(9)	59(7)	-24(7)	-18(6)	11(7)
C(31B)	47(7)	92(10)	61(7)	-26(7)	-4(6)	-4(7)
C(32B)	53(7)	64(7)	52(6)	-18(5)	-10(5)	1(5)
C(33B)	44(6)	52(6)	45(5)	-3(5)	0(4)	-5(5)
C(34B)	58(7)	50(6)	67(7)	-11(5)	3(6)	-21(5)
C(35B)	57(7)	42(6)	77(8)	8(5)	-9(6)	-19(5)
C(36B)	65(8)	50(7)	74(8)	10(6)	-9(6)	-2(6)

C(37B)	59(7)	69(8)	58(7)	-4(6)	-17(6)	-7(6)
C(38B)	54(7)	46(6)	50(6)	-2(5)	-9(5)	-8(5)

Table 8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

	x	y	z	U(eq)
H(1A)	11716	6402	1277	60
H(4A)	12387	4641	1455	77
H(5A)	14451	3429	1426	86
H(6A)	15626	3043	602	85
H(7A)	14781	3882	-248	78
H(8A)	12702	5157	-249	71
H(10A)	12065	6791	-392	65
H(11A)	11297	7524	-1268	81
H(12A)	9101	7717	-1445	78
H(13A)	7600	7172	-740	73
H(14A)	8297	6426	132	66
H(16A)	11713	7379	1966	121
H(17A)	12773	8447	2131	184
H(18A)	11861	10106	1802	232
H(19A)	10110	10638	1283	203
H(20A)	9013	9650	1073	151
H(22A)	9583	8887	255	112
H(23A)	7877	9606	-383	150
H(24A)	5875	9226	-233	132
H(25A)	5324	8269	576	131
H(26A)	6867	7607	1243	89
H(1B)	9331	8367	3887	61
H(4B)	9238	5218	4196	70
H(5B)	11366	4064	4061	85
H(6B)	13144	4469	3507	93
H(7B)	12944	6053	3055	89
H(8B)	10750	7227	3144	89
H(10B)	8061	6079	4900	71
H(11B)	6313	5584	5458	81
H(12B)	4219	5967	5129	88
H(13B)	3811	6859	4248	82

H(14B)	5509	7388	3678	65
H(16B)	8338	8143	5513	56
H(17B)	7402	7516	6382	66
H(18B)	5193	7418	6507	69
H(19B)	3858	7913	5739	69
H(20B)	4798	8612	4872	61
H(22B)	7632	9832	5309	60
H(23B)	8410	11142	5289	68
H(24B)	9268	11927	4439	74
H(25B)	9343	11411	3620	72
H(26B)	8454	10183	3622	71

4. Complex [Au₂{(PPh₂)₂CCN}₂] (5)

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	9266(1)	160(1)	5796(1)	38(1)
P(1)	10300(1)	-1068(1)	6447(1)	36(1)
P(2)	8027(1)	1346(1)	5210(1)	37(1)
N(1)	6834(5)	2668(3)	3249(3)	50(1)
C(1)	8188(5)	1454(3)	4072(3)	37(1)
C(2)	7435(5)	2122(4)	3631(3)	40(1)
C(3)	6212(5)	1218(3)	5503(3)	37(1)
C(4)	5890(5)	1131(4)	6394(4)	46(1)
C(5)	4545(6)	997(4)	6646(4)	53(1)
C(6)	3501(6)	965(4)	6030(4)	54(1)
C(7)	3796(6)	1054(4)	5163(4)	53(1)
C(8)	5165(5)	1178(4)	4887(4)	44(1)
C(9)	8506(5)	2405(4)	5723(3)	40(1)
C(10)	9860(6)	2515(4)	6058(4)	48(1)
C(11)	10263(7)	3331(5)	6386(4)	60(2)
C(12)	9380(8)	4047(4)	6373(4)	65(2)
C(13)	8033(7)	3943(4)	6054(4)	58(2)
C(14)	7610(6)	3130(4)	5727(3)	45(1)
C(15)	9041(5)	-1978(4)	6491(3)	40(1)
C(16)	9332(6)	-2813(4)	6144(4)	48(1)
C(17)	8331(7)	-3481(4)	6135(4)	58(2)
C(18)	7040(7)	-3319(5)	6477(4)	60(2)
C(19)	6734(6)	-2497(5)	6821(4)	57(2)
C(20)	7728(5)	-1822(4)	6831(3)	49(1)
C(21)	10713(5)	-865(3)	7589(3)	37(1)
C(22)	10732(5)	-1563(4)	8187(3)	44(1)
C(23)	11064(6)	-1398(4)	9053(4)	49(1)

C(24)	11340(6)	-542(4)	9323(4)	52(1)
C(25)	11346(7)	159(4)	8736(4)	55(2)
C(26)	11017(6)	-1(4)	7863(4)	45(1)

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	36(1)	41(1)	35(1)	2(1)	1(1)	5(1)
P(1)	34(1)	41(1)	34(1)	2(1)	0(1)	1(1)
P(2)	35(1)	40(1)	35(1)	0(1)	0(1)	2(1)
N(1)	48(3)	49(3)	52(3)	5(2)	-4(2)	7(2)
C(1)	34(2)	40(3)	36(2)	3(2)	-1(2)	4(2)
C(2)	38(3)	42(3)	39(2)	-3(2)	2(2)	0(2)
C(3)	35(2)	35(2)	41(3)	1(2)	3(2)	0(2)
C(4)	43(3)	51(3)	46(3)	-2(2)	3(2)	2(2)
C(5)	52(3)	57(4)	49(3)	0(3)	13(3)	-1(3)
C(6)	39(3)	53(3)	70(4)	4(3)	10(3)	0(2)
C(7)	37(3)	58(3)	64(4)	7(3)	-5(3)	-3(2)
C(8)	38(3)	49(3)	47(3)	4(2)	-3(2)	-1(2)
C(9)	46(3)	43(3)	32(2)	1(2)	0(2)	-3(2)
C(10)	40(3)	56(3)	47(3)	1(2)	0(2)	-2(2)
C(11)	52(3)	69(4)	59(4)	-1(3)	-9(3)	-14(3)
C(12)	85(5)	49(4)	62(4)	1(3)	-16(3)	-15(3)
C(13)	70(4)	48(3)	57(3)	5(3)	-10(3)	3(3)
C(14)	50(3)	42(3)	43(3)	2(2)	-5(2)	2(2)
C(15)	34(2)	51(3)	34(2)	2(2)	0(2)	-4(2)
C(16)	47(3)	49(3)	49(3)	5(3)	-4(2)	-5(2)
C(17)	68(4)	53(4)	54(3)	1(3)	-8(3)	-16(3)
C(18)	58(4)	73(4)	50(3)	7(3)	-9(3)	-28(3)
C(19)	39(3)	88(5)	44(3)	10(3)	-4(2)	-10(3)
C(20)	42(3)	60(3)	44(3)	5(2)	1(2)	-3(2)
C(21)	33(2)	42(3)	36(2)	0(2)	1(2)	4(2)
C(22)	45(3)	42(3)	44(3)	1(2)	-3(2)	-2(2)
C(23)	48(3)	54(3)	44(3)	11(2)	-5(2)	0(3)
C(24)	54(3)	62(4)	39(3)	-2(3)	-8(2)	5(3)
C(25)	67(4)	49(4)	49(4)	-8(2)	-5(3)	0(3)
C(26)	52(3)	43(3)	39(3)	5(2)	0(3)	1(2)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**.

	x	y	z	U(eq)
H(4)	6603	1165	6820	56
H(5)	4331	927	7247	63
H(6)	2571	879	6211	65
H(7)	3069	1033	4744	63
H(8)	5372	1234	4283	53
H(10)	10489	2026	6057	57
H(11)	11165	3399	6625	72
H(12)	9681	4613	6580	78
H(13)	7410	4434	6062	70
H(14)	6699	3064	5503	54
H(16)	10223	-2930	5911	58
H(17)	8538	-4051	5892	70
H(18)	6359	-3778	6474	72
H(19)	5841	-2386	7055	68
H(20)	7509	-1252	7069	59
H(22)	10518	-2154	8002	52
H(23)	11099	-1878	9460	59
H(24)	11531	-430	9922	62
H(25)	11572	747	8926	66
H(26)	11000	479	7457	54