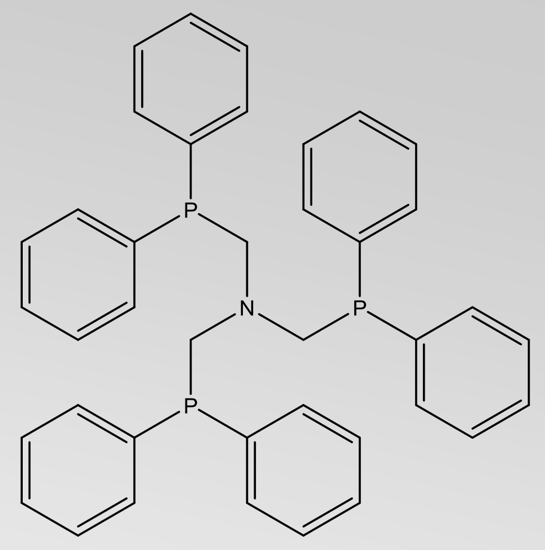
Imperial College London

Department of Chemistry

synthesis and characterisation of
ligand-supported gold complexes and clusters

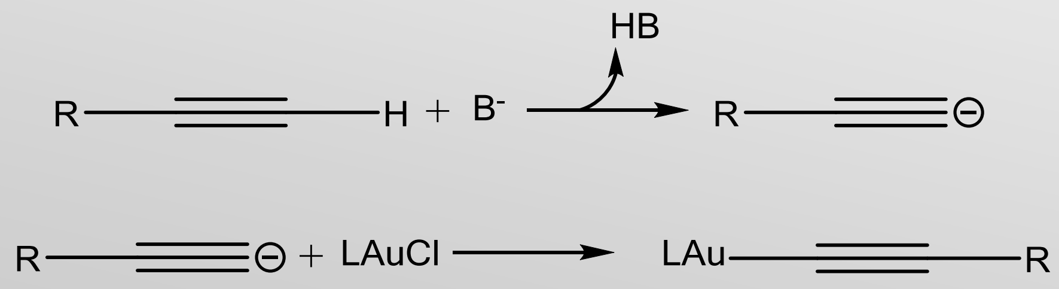
a 3rd year BSc research project by **Jacques Smith** with supervision by **Dr. Philip Miller**

1. an introduction


N-triphos

The **triphos** series of ligands are **tridentate** ligands, usually with three phosphorus atoms joined through an alkyl bridge to a central atom. They have been studied in co-ordination chemistry and nitrogen-centred triphos ligands have been a recent development.

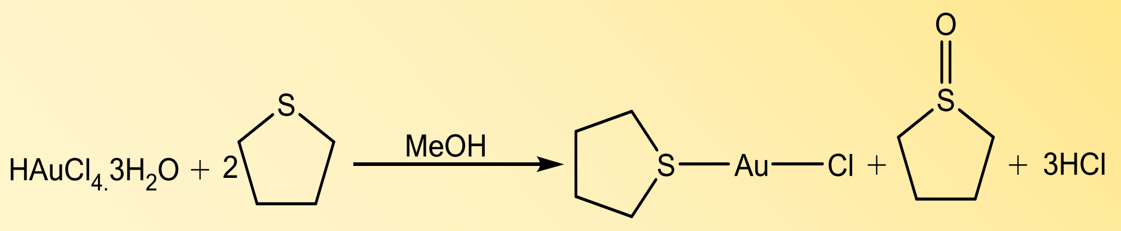
Gold clusters of a moderate number of atoms (usually 11 atoms but clusters of up to 55 atoms have been observed) supported by phosphine molecules have been synthesised recently and an attempt at synthesising similar clusters supported by triphos ligands.



The affinity of Au(I) ions to **acetylides** have been well known for some time and an attempt to synthesise gold acetylides supported by triphos ligands has also been made.

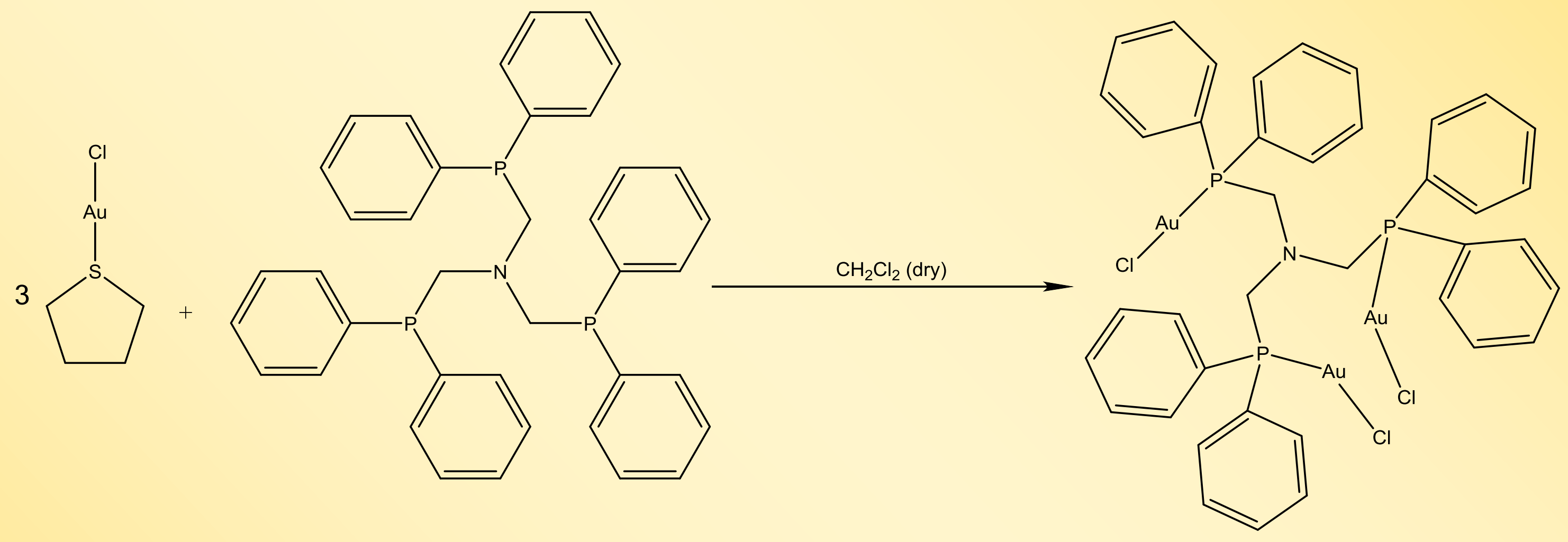
2. synthesis of $Au_3[N\text{-triphos}^{Ph}]Cl_3$

A gold complex precursor, Au(tht)Cl, was first synthesised, as a stepping stone.

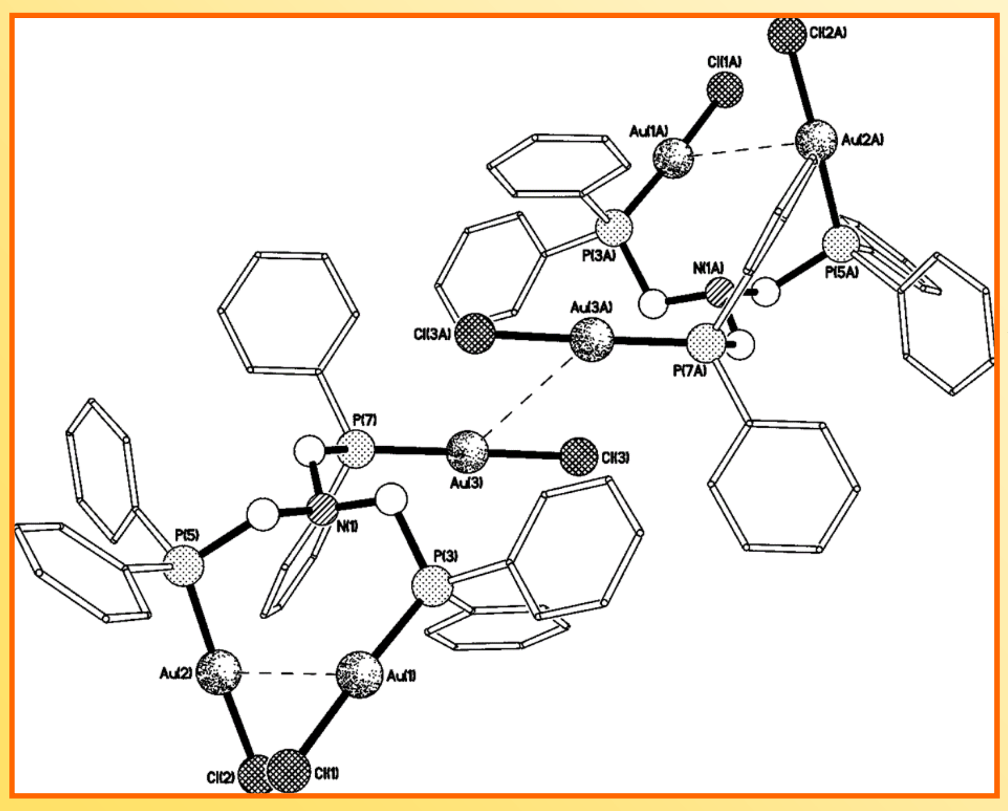


This reaction is high-yielding, with yields of **96%** achieved.

This precursor was subsequently reacted with the N-triphos^{Ph} ligand, in a **3:1 ratio** of precursor and ligand under an atmosphere of nitrogen:



This reaction is not as high-yielding, with only a **46% yield** achieved overall.



X-Ray suitable crystals were obtained through recrystallization with an acetone/diethyl ether system

A crystal structure was obtained and the compound was observed to exist as a dimer in the solid state.

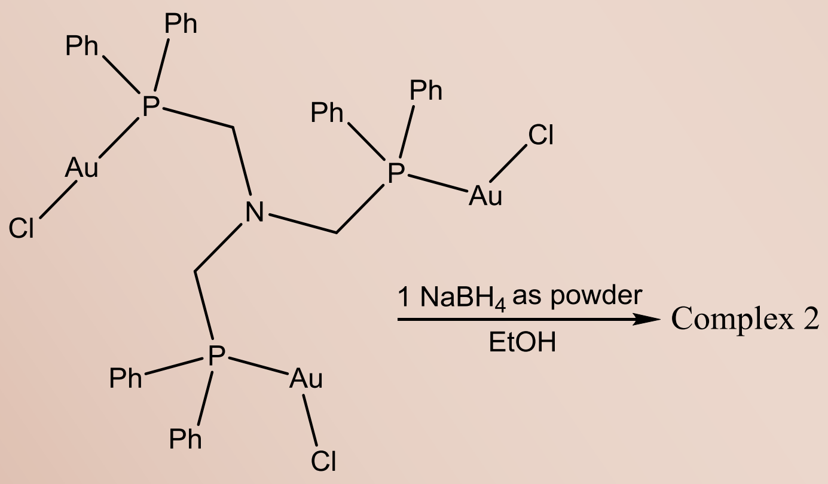
The ^1H NMR, $^{31}P\{^1H\}$ NMR and mass spectra are in agreement with the structure of the compound overall.

3. synthesis of gold clusters

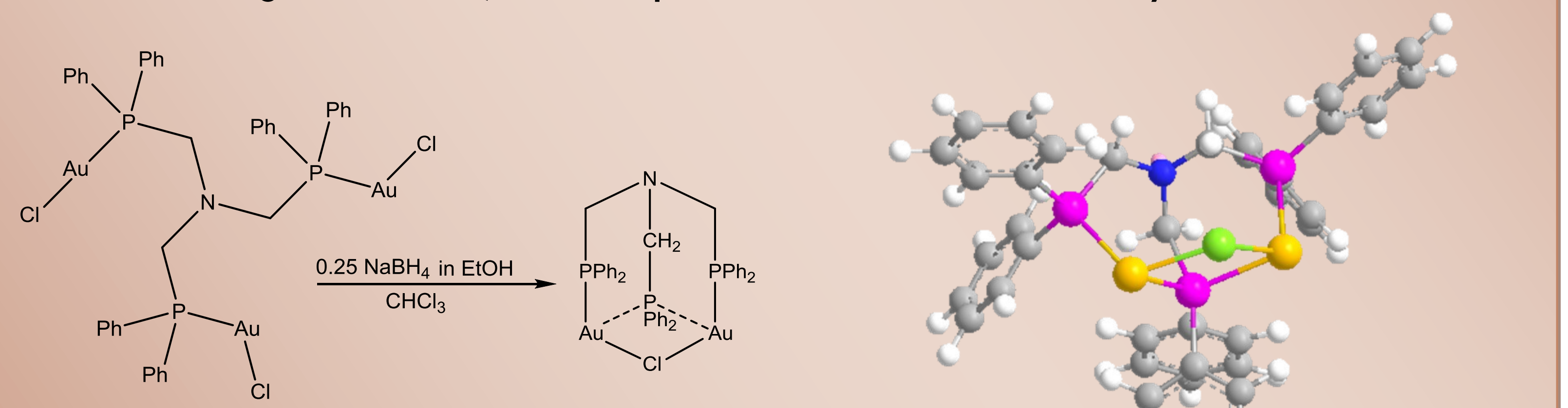
Gold clusters have been known to be formed from the reduction of gold (I) chlorides with reducing agents.

The general theme was the reduction of the $Au_3[N\text{-triphos}^{Ph}]Cl_3$ with $NaBH_4$. **Three different ratios** of precursor to $NaBH_4$ were explored, and as expected, **three different outcomes** were achieved. These reactions were performed in an **inert atmosphere.** All solids obtained were **brown** in appearance and **free-flowing.**

1 equivalent of $NaBH_4$ yielded a compound with **5** peaks in its $^{31}P\{^1H\}$ NMR spectrum, which led to the possibility of a **mixture of products.** A reasonable attempt at determining the structure was not possible as there was not enough useful information obtained from the spectroscopy, and no X-ray suitable crystals were successfully grown from the compound.



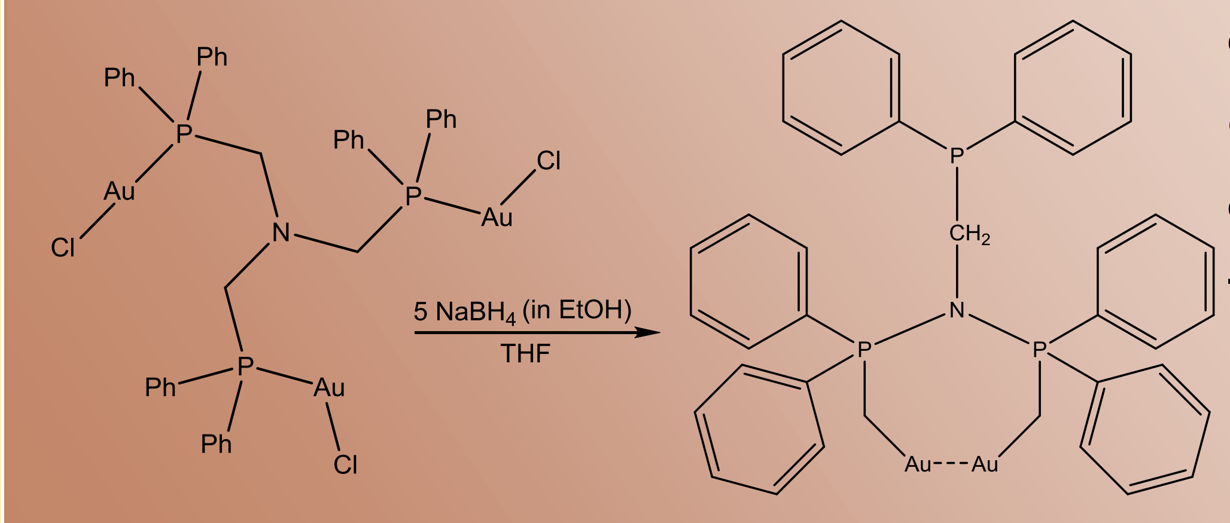
0.25 equivalent of $NaBH_4$ leads to an **incomplete reduction** of the gold precursor—meaning that the cluster compound still contained **chlorine**, as confirmed through the relevant peaks in the mass spectrum. There may possibly be a **bridging chloride** between two gold atoms, such a phenomenon has recently been observed.



Above: Reaction scheme, proposed structure and 3D rendering of product:

White = H; Grey = C; Blue = N; Magenta = P; Green = Cl; Gold = Au.

5 equivalents of $NaBH_4$ leads to a **full reduction** of the gold precursor and confirmed by mass spectroscopy, **no chlorine** was present in this gold complex. The proposed structure through the analysis of the NMR and mass spectra contains an **aurophilic interaction.**



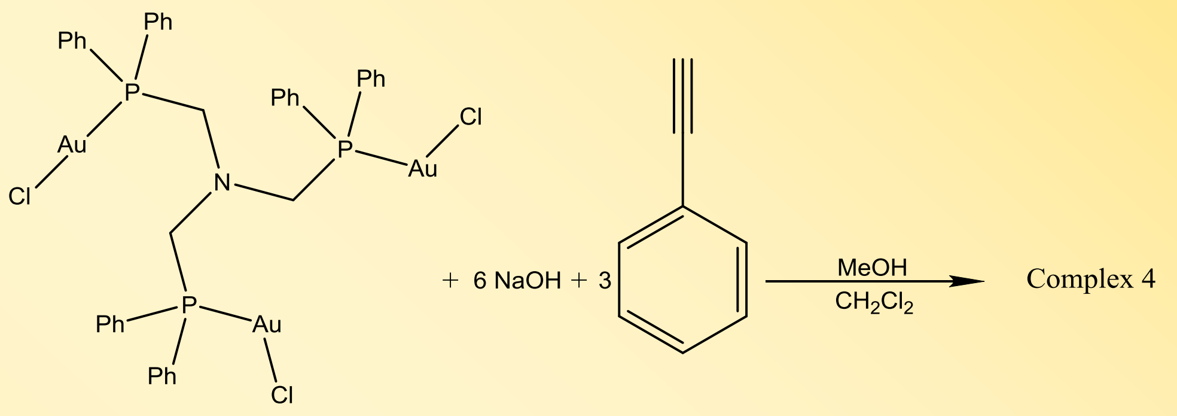
4. synthesis of gold acetylide complexes

The reduction of the $Au_3[N\text{-triphos}^{Ph}]Cl_3$ precursor was reacted with phenylacetylene to form new complexes. These complexes were **stable** in the **solid state**, but were **unstable in solution**. Because of this, only mass spectra were successfully recorded.

Interestingly, two different methods yielded **two different compounds** which were **different** in appearance. These reactions were performed in inert conditions.

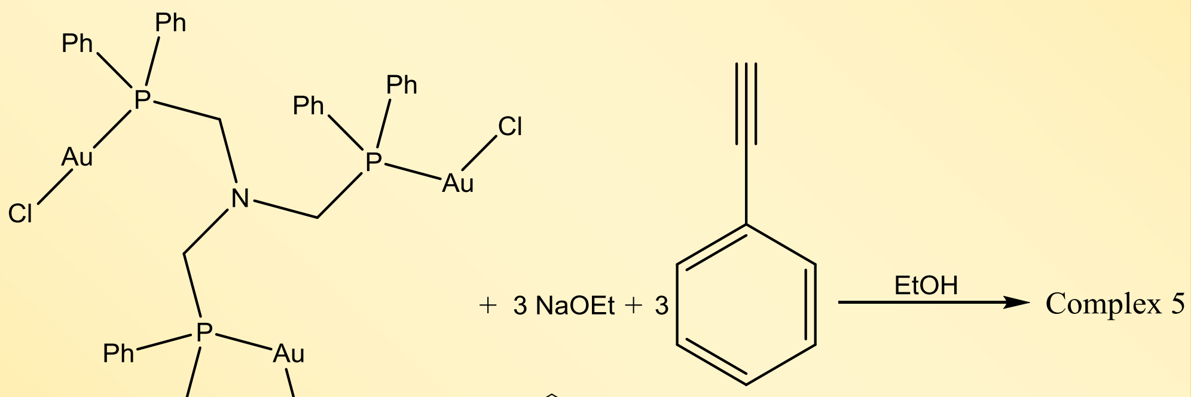
METHOD 1: Yields a **yellow** solution which become **pink** over time—a **pink solid** retrieved.

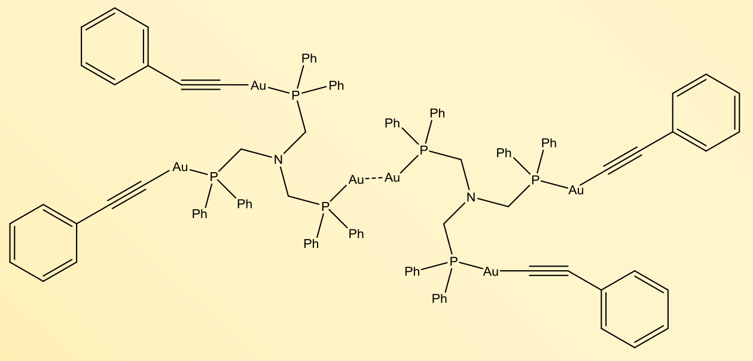
Not enough data to work out the structure.



METHOD 2: Yields a **yellow solid.** There is not enough data to work out the structure.

There are possibly **aurophilic interactions** between two molecules to form a dimer, as with the precursor, as seen on the right.





5. conclusion

- A new gold compound, $Au_3[N\text{-triphos}^{Ph}]Cl_3$ has **successfully** been synthesised and characterised; the N-triphos^{Ph} ligand co-ordinates effectively to Au(I).
- However, when reducing this compound with $NaBH_4$, clusters did **not** successfully form; most likely to the **rigidity** and **steric hindrance** of the N-triphos^{Ph} ligand.
- The synthesis and characterisation of the **gold acetylide complexes** supported by the N-triphos^{Ph} ligand proved to be **unsuccessful.**