

New Routes for Preparation and Characterization of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ Complex

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(Received: 28 February 2011;

Accepted: 9 August 2012)

AJC-11946

The gold complex *i.e.*, $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ has been successfully produced by three reactions, the reaction of polymeric gold cyanide $[\text{Au}(\text{CN})]_n$ with a suspension of *bis*(diphenylphosphino)methane (dppm), in acetone in a 2:1, pure ammonia (NH_3), $[\text{Au}(\text{C}\equiv\text{N})]_n$ and $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ in acetone in a 2:2:1 or that of $[\text{Au}(\text{C}\equiv\text{N})(\text{NH}_3)_2]$ with $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ in acetone in a 1:0.5 giving a white precipitate collected as $\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2$. The complex was characterized by elemental analysis, FT-IR and NMR spectroscopy and found in agreement with the proposed formula $\text{C}_{27}\text{H}_{22}\text{N}_2\text{P}_2\text{Au}_2$.

Key Words: $[\text{Au}(\text{CN})]_n$, Gold complexes, Gold Cyanide, *Bis*(diphenylphosphino)methane.

INTRODUCTION

Diphosphine ligand plays an important role in transition metals, also becomes more interest in fundamental and applied chemistry as a result of the importance of its complexes. A *bis*(diphenylphosphino)methane (dppm) well known to act as bidentate ligand (bridging ligand) between transition metals an example $\text{M}_2(\mu\text{-dppm})^{1,2}$. The ability of the dppm to span a wide range of metal-metal distances and hold the metal atoms in mutual proximity through the course of reactions becomes popular choice ligand in the development of di- and polynuclear transition-metal chemistry, perhaps most notably in the rich chemistry of the complexes lead to $\mu\text{-dppm}$ ligand³.

Recent investigations concerning the reactions of gold, silver and other metals with diphos that are closely related to the subject have been studied⁴⁻¹⁴.

In cyanide-metal complexes, cyanide bonds to the metal by a strong σ -donation and possibly by π -back donation in which the metal *d* orbitals interact with the empty π^* orbitals of the $\text{C}\equiv\text{N}^-$ ligands. The two metals have d^{10} configuration heavy metal ions Au^+ and Ag^+ . Dicyanoaurates(I) and dicyanoargentates(I) are representatives of linear two coordinate complexes, thereby attracting much attention on their molecular, electronic structures and other properties. On the other hand, the formation of $\text{Au}(\text{C}\equiv\text{N})_2^-$ and $\text{Ag}(\text{C}\equiv\text{N})_2^-$ complexes has been widely used in gold industry for the extraction of gold and silver from ores, followed by adsorption on activated carbon. $\text{Au}(\text{C}\equiv\text{N})_2^-$ and $\text{Ag}(\text{C}\equiv\text{N})_2^-$ complexes also find a wide application in the gold and silver electroplating industry¹⁵⁻¹⁷.

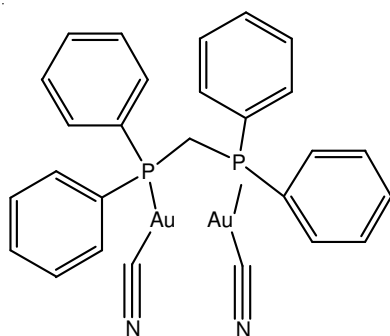
The complex $[\text{Au}(\text{C}\equiv\text{N})]_n$ was prepared as described in ref.¹⁸. It is well known that cyanide ligand $\text{C}\equiv\text{N}$ is similar to acetylide ligand $\text{C}\equiv\text{C-R}$ in some aspects¹⁹, but behaved different in others, an example the cyanide has a lone pair of electrons on the nitrogen atom. In addition the triple bond $\text{C}\equiv\text{N}$ is rarely used in π -bonding this is in sharp contrast to the alkyne's multiples bonds²⁰.

Al-Ohaly²¹ has reported the preparation of cyanohalogeno complexes of gold (I) and their reaction with triphenylphosphine (PPh_3) to form $[\text{AuCNX}]$ type complexes *viz.*, $[\text{N}(\text{PPh}_3)_2]_2[\text{Au}(\text{C}\equiv\text{N})\text{Cl}]$, $[\text{PPh}_4][\text{Au}(\text{C}\equiv\text{N})\text{Br}]$ and $[\text{N}(\text{PPh}_3)_2][\text{Au}(\text{C}\equiv\text{N})\text{I}]$. Recently, Eduardo *et al.*²² have reported the quite eight-electron donor of gold and δ ppm. They also reported the preparation of $\text{NEt}_4[\text{Au}(\text{mes})\text{Cl}]$ and $[\text{NPPPh}_3][(\text{mes})\text{Au}(\text{CN})\text{Au}(\text{mes})]^{23}$, in a different report by Michael *et al.*²⁴ they have reported the preparation and X-ray spectral characterization of $[\text{Au}(\text{NH}_3)_2]$ and $[\text{Au}(\text{NH}_3)_2]\text{Br}$.

In another report, David *et al.*²⁵ prepared $[\text{Au}_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ and characterized it by single X-ray diffraction. This compound is similar to the compound that we have prepared here except for the cyanide ligands in which the two gold atoms were attached, but they have used different routes.

The spectrochemistry of ligation of gold(I) by cyanide in liquid ammonia has been investigated by Gans and co-worker²⁶.

We have reported that the title complex $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ has been produced by three different ways. It is dependent on of the molar ratio of the reactants giving a white precipitate as **Scheme-I**:

Scheme-1: Complex $[\text{Au}_2(\text{CN})_2(\text{dppm})]$

EXPERIMENTAL

All chemicals used in the experiments were of AnalaR grade. Hexane was dried and distilled before use; acetone was kept over molecular sieves and used without distillation are all from (BDH). The complex $[\text{Au}(\text{CN})]_n$ was prepared as described¹⁸. The NMR spectra were recorded by Jeol-Eclipse 400 FT-NMR and elemental analysis by Perkin Elmer Series II CHNS/O analyzer 2400. Metal analysis was carried out at Pascher's Microanalytical Laboratory.

FT-IR spectra were recorded by prestige -21-FT-IR spectrophotometer-shimadzo (over the range 4000-400 cm^{-1}).

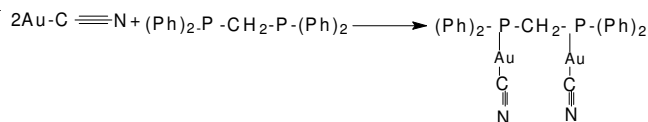
Preparation of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{dppm}]$: The gold cyanide polymer (0.446 g, 2 mmol) was added to a clear solution of *bis*(diphenylphosphino)methane $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ (0.384g, 1 mmol) in acetone (25 cm^3). Immediate after 5 min the gold complex disappeared and a clear solution was obtained. Addition of hexane (50 cm^3) to the filtrate gave a white compound. The precipitate filtered off, washed with acetone/hexane and hexane and collected as $\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2$ m.p. 175 °C; found (%): C, 39.33; H, 2.67, N, 3.16. $\text{C}_{27}\text{H}_{22}\text{N}_2\text{P}_2\text{Au}_2$ required; C, 39.04; H, 2.65, N 3, 37). (disc, KBr, ν_{max} , cm^{-1}): 2137 ($\text{C}\equiv\text{N}$).

Preparation of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{dppm}]$: The pure ammonia (30 cm^3) was condensed (at -45 °C) onto polymeric gold cyanide of $\text{AuC}\equiv\text{N}$ (0.446 g, 2 mmol). The colour of the solid changed from yellow to white and a colourless solution was obtained. So the *bis*(diphenylphosphino)methane(diphos) (0.384 g, 1 mmol) was then added to the solution. Stirring was continued for 10 min under nitrogen to discard ammonia and reach dryness. The white residue was dissolved in acetone (30 cm^3) and a clean solution was obtained. The addition of hexane (50 cm^3) to the solution gave a white precipitate of $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2\text{Au}_2(\text{C}\equiv\text{N})_2$ (0.745 g, 89.8 %). m.p. 180 °C; found (%): C, 39.72; H, 2.73; N, 3.16. $\text{C}_{27}\text{H}_{22}\text{Au}_2\text{N}_2\text{P}_2$ required; C, 39.04; H, 2.65; N 3, 37) (disc, KBr, ν_{max} , cm^{-1}) 2137 ($\text{C}\equiv\text{N}$).

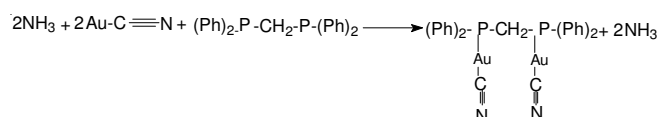
Preparation of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{dppm}]$: The gold cyanide monoammoniate (0.240 g, 1 mmol) was added to the suspension of *bis*(diphenyl phosphino)methane, $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ (0.192 g, 0.5 mmol) in acetone (25 cm^3). The colour changed to pale yellow. Stirring was continued and after 20 min, a clear solution was obtained. The volume was reduced under vacuum to 10 cm^3 . A white precipitate was formed and collected as $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2\text{Au}_2(\text{C}\equiv\text{N})_2$ (0.330 g, 79.5 %) m.p. 186 °C; (found (%) C, 38.83; H, 2.46, N, 2.93, $\text{C}_{27}\text{H}_{22}\text{Au}_2\text{N}_2\text{P}_2$ required; C, 39.04; H, 2.65; N, 3.37). (disc, KBr, ν_{max} , cm^{-1}): 2137 ($\text{C}\equiv\text{N}$).

RESULTS AND DISCUSSION

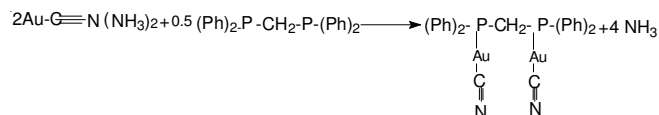
The addition of $(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ to $[\text{AuC}\equiv\text{N}]_n$ in a 1:2 in acetone gave a clear solution. Normal workup resulted in a white precipitation of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ as in method (a) as presented here.



In method (b), $[\text{AuC}\equiv\text{N}]_n$ has been added to the condensed ammonia at -45 °C. The colour changed from yellow to white. $\text{A}(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2$ was then added to the suspended solution in a 2:2:1 ammonia gas was discarded by evaporation with nitrogen gas and vacuum suction. The new complex $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ was then isolated with acetone as (b):



In method (c), the complex $[\{\text{Au}(\text{C}\equiv\text{N})(\text{NH}_3)_2\}]$ has been prepared and characterized as mentioned in reference¹¹, in which the prepared complex was added to the suspension solution of diphos in a 1:0.5 in acetone. The reaction resulted in a white precipitate of the complex $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$ this is known as method (c).



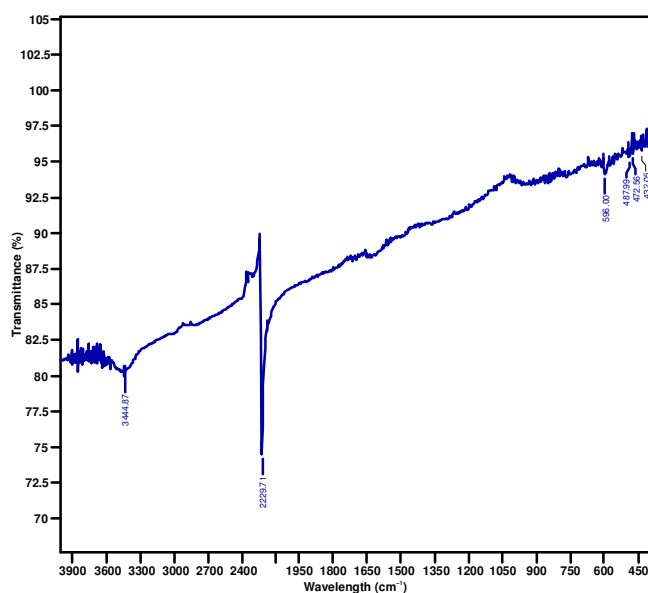
It is deduced that both methods (b and c) are well suited for the reactions of metal polymers, such as, $[\text{AuC}\equiv\text{N}]_n$, $[\text{AgC}\equiv\text{N}]_n$ and $[\text{CuC}\equiv\text{N}]_n$ or $[\text{AuC}\equiv\text{C}]_n$ or $[\text{AgC}\equiv\text{C}]_n$ or $[\text{CuC}\equiv\text{C}]_n$, which are insoluble in known organic solvents. The ammonia group in all these complexes can easily be substituted by another group in the solution and discarded as mentioned previously. The bond between the complexes prepared in ammonia is very weak.

Elemental analysis agrees very well with this formulation (Table-1):

TABLE-1
ANALYTICAL DATA

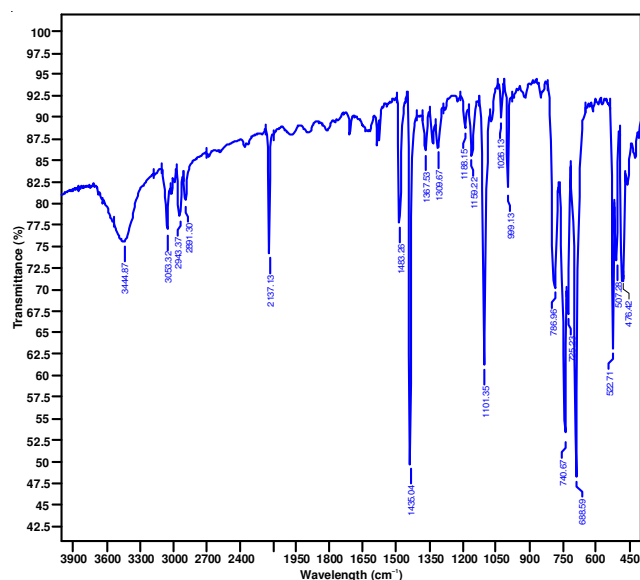
Complex	Found (%) (required)			Metal analysis (%)	m.p. (°C)
	C	H	N	Au	
(a) $\text{Au}_2(\text{C}\equiv\text{N})_2$ dppm	39.33 (39.04)	2.56 (2.65)	3.16 (3.37)	46.5 (47.45)	178
(b) $\text{Au}_2(\text{C}\equiv\text{N})_2$ dppm	39.72 (39.04)	2.73 (2.65)	3.16 (3.37)	47 (47.45)	180
(c) $\text{Au}_2(\text{C}\equiv\text{N})_2$ dppm	38.83 (39.04)	2.46 (2.65)	2.93 (3.37)	46.2 (47.45)	186

IR and NMR spectra: The FT-IR (KBr disc) (Fig. 1) vibrational band assigned to the ($\text{C}\equiv\text{N}$) stretch was lower by

Fig. 1. Spectrum FT-IR of $[\text{AuC}\equiv\text{N}]_n$

ca. 92.58 cm^{-1} compared with that observed for in $[\text{AuC}\equiv\text{N}]_n$ and appeared very strong at *ca.* 2137 cm^{-1} in the spectra of all three methods (a, b and c).

Fig. 2, such difference is probably due to an increase in the metal-carbon π -bonding which increases the Au-C force constant lowering $\nu(\text{C}\equiv\text{N})$ bond order²⁷, which in turn lowers to a great extent the $\nu(\text{C}\equiv\text{N})$ vibrational frequency down to 2137 cm^{-1} . A very strong band at 1101 cm^{-1} was assigned to P-C

Fig. 2. Spectrum FT-IR of $[\text{Au}_2(\text{C}\equiv\text{N})_2\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2]$

The proposed structure is in accordance with ^1H , ^{13}C and ^{31}P NMR spectrum. The ^{31}P NMR (CDCl_3) spectrum indicates a single peak at 35.7 (ppm), this represents two equivalent

4-coordinate P atoms. The ^1H NMR (CDCl_3) spectrum shows a single peak at 1.86 δ (ppm) this represents the methylene protons adjacent to the phosphorous atoms and a multiplet peaks spread over 7.23-7.60 δ (ppm) ($J = 6.84\text{ Hz}$) assigned to 20 aromatic protons. The ^{13}C NMR (CDCl_3) spectrum indicates a peak at 26.49 δ (ppm) assigned to the $-\text{CH}_2-$ carbon, a peak at 151.52 δ (ppm) represents the $-\text{C}\equiv\text{N}$ carbon, while the aromatic carbons are represented by the peaks 128.49-133.47 δ (ppm).

ACKNOWLEDGEMENTS

The authors are grateful to King Saud University, Deanship of Scientific Research College of Science Research Center for supporting this project.

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