Journal of Organometallic Chemistry 758 (2014) 9–18

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, spectral and structural studies of silver and gold(I) complexes containing some symmetrical diphosphine ligands

Manoj Trivedi [a,*], Bhaskaran [a], Gurmeet Singh [a], Abhinav Kumar [b], Nigam P. Rath [c,**]

[a] *Department of Chemistry, University of Delhi, Delhi 110007, India*
[b] *Department of Chemistry, University of Lucknow, Lucknow 226007, India*
[c] *Department of Chemistry & Biochemistry and Centre for Nanoscience, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121-4499, USA*

ARTICLE INFO

Article history:
Received 28 January 2014
Accepted 31 January 2014

Keywords:
Diphosphine
Silver complex
Gold complex
X-ray
Weak interaction

ABSTRACT

New silver(I) and gold(I) complexes $[\mathrm{Ag_3}(\mu_2\text{-CN})_3(\kappa^2\text{-}P,P\text{-dppf})_2]_n\cdot\mathrm{C_6H_{12}}$ (**1**), $[\mathrm{Ag_4}(\mu_2\text{-CN})_4(\kappa^1\text{-}P,P\text{-dtbpf})]_n$ (**2**), $[\mathrm{Au_2}(\mu_1\text{-CN})_2(\kappa^1\text{-}P,P\text{-dppf})]$ (**3**), $[\mathrm{Au_2}(\mu_1\text{-CN})_2(\kappa^1\text{-}P,P\text{-dtbpf})]$ (**4**), $[\mathrm{Ag_4}(\mu_3\text{-CN})_2(\mu_1\text{-CN})_2(\kappa^1\text{-}P,P\text{-dcpf})_2]$ (**5**), and $[\mathrm{Au_2}(\mu_1\text{-CN})_2(\kappa^1\text{-}P,P\text{-dcpf})]$ (**6**) were prepared starting with MCN (M = Ag, Au) and dppf/dtbpf/dcpf (dppf = 1,1′-bis(diphenylphosphino) ferrocene; dtbpf = 1,1′-bis(di-*tert*-butylphosphino) ferrocene; dcpf = 1,1′-bis(dicyclohexylphosphino) ferrocene) in 1:1 M ratio in DCM:MeOH (50:50 V/V) at room temperature. The resulting complexes have been characterized by elemental analysis, IR, ^{1}H & ^{31}P NMR, ESI-MS and electronic absorption spectroscopy. Molecular structures for the complexes **1**, **2**, **5**, and **6** were determined crystallographically. Complex **1** and **2** exist as an infinite one-dimensional (1D) polymeric chain constructed by $[(\mu_2\text{-CN})\mathrm{Ag}(\mu_2\text{-CN})\mathrm{Ag}]$ fragments bridged *via* dppf/dtbpf ligands. The molecular structure of **5** reveals a centrosymmetric dimeric complex in which the two silver atoms are bonded to two dcpf ligands in κ^1 manner and two cyanide groups in a μ_3 bonding mode to generate nearly planar $\mathrm{Ag_2}(\mu_3\text{-CN})_2$ framework, while complex **6** exists in open bridging mode containing Au atoms in ideal linear coordination defined by *P,CN*-donor sets.

1. Introduction

Ferrocene-based phosphines have emerged as one of the most powerful classes of ligands in chiral and achiral catalysis [1–10]. Although there are many different types of ferrocenyl diphosphines, the most common are 1,1′-bis(diphenylphosphino) ferrocene (dppf) [11–25] and 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) [19,26]. These ligands have significant advantages over other diphosphines which contain alkyl, rather than metallocene, backbones [27]. There are several reports available on dppf [28–36] and a few on dtbpf [19,26,37–42] and dcpf [27,43]. Compared to the significant amount of work on dppf itself, dtbpf and dcpf have received surprisingly little attention. Recently another incentive to study silver and gold complexes of bis(phosphino)ferrocenes, are of particular interest on account of the potential of their compounds as biologically active agents [44], catalysts [45] and luminescent materials [46–49]. Previous work on the coinage metals, especially $\mathrm{Ag^+}$, revealed a large variety of mono-, di- and polynuclear structures that can be assembled from dppf [3,28,29,50]. The structural outcome is generally hard to predict due to the numerous permutations arising from the flexible metal geometry (linear ↔ trigonal planar ↔ tetrahedral), dppf bonding (unidentate ↔ bridging ↔ chelating) and coordination state of the supporting anion (halide, pseudohalide etc.) (uncoordinated ↔ terminal ↔ bridging ↔ chelating ↔ capping). Our current understanding on $[\mathrm{AgX(dppf)}]_n$ [29–31] and $[\mathrm{AuX(dppf)}]_n$ [51–55] complexes is that they generally prefer dimeric and polymeric structures. Several variations are known depending on the interaction of the dppf and $\mathrm{X^-}$ but few reports are published till date related to dtbpf/dcpf and $\mathrm{X^-}$. The dppf based complexes are commonly prepared from direct addition of MX to dppf using stoichiometric conditions of 1:1. During the course of our current study concerning interaction of MCN (M = Ag, Au) with dppf/dtbpf/dcpf, and to assist our understanding of the Ag(I) and Au(I) species present in solid and solution state, herein we report the synthesis, spectroscopic characterization, and structural studies of representative silver(I) and gold(I) complexes $[\mathrm{Ag_3}(\mu_2\text{-CN})_3(\kappa^2\text{-}P,P\text{-dppf})_2]_n\cdot\mathrm{C_6H_{12}}$ (**1**), $[\mathrm{Ag_4}(\mu_2\text{-CN})_4(\kappa^1\text{-}P,P\text{-dtbpf})]_n$ (**2**)], $[\mathrm{Ag_4}(\mu_3\text{-}$

---

* Corresponding author. Tel.: +91 (0) 9811730475.
** Corresponding author. Tel.: +1 314 516 5333.
E-mail addresses: manojtri@gmail.com (M. Trivedi), rathn@umsl.edu (N.P. Rath).

http://dx.doi.org/10.1016/j.jorganchem.2014.01.037
0022-328X/

$CN)_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dcpf})_2]$ (**5**) and $[Au_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dcpf})]$ (**6**), respectively.

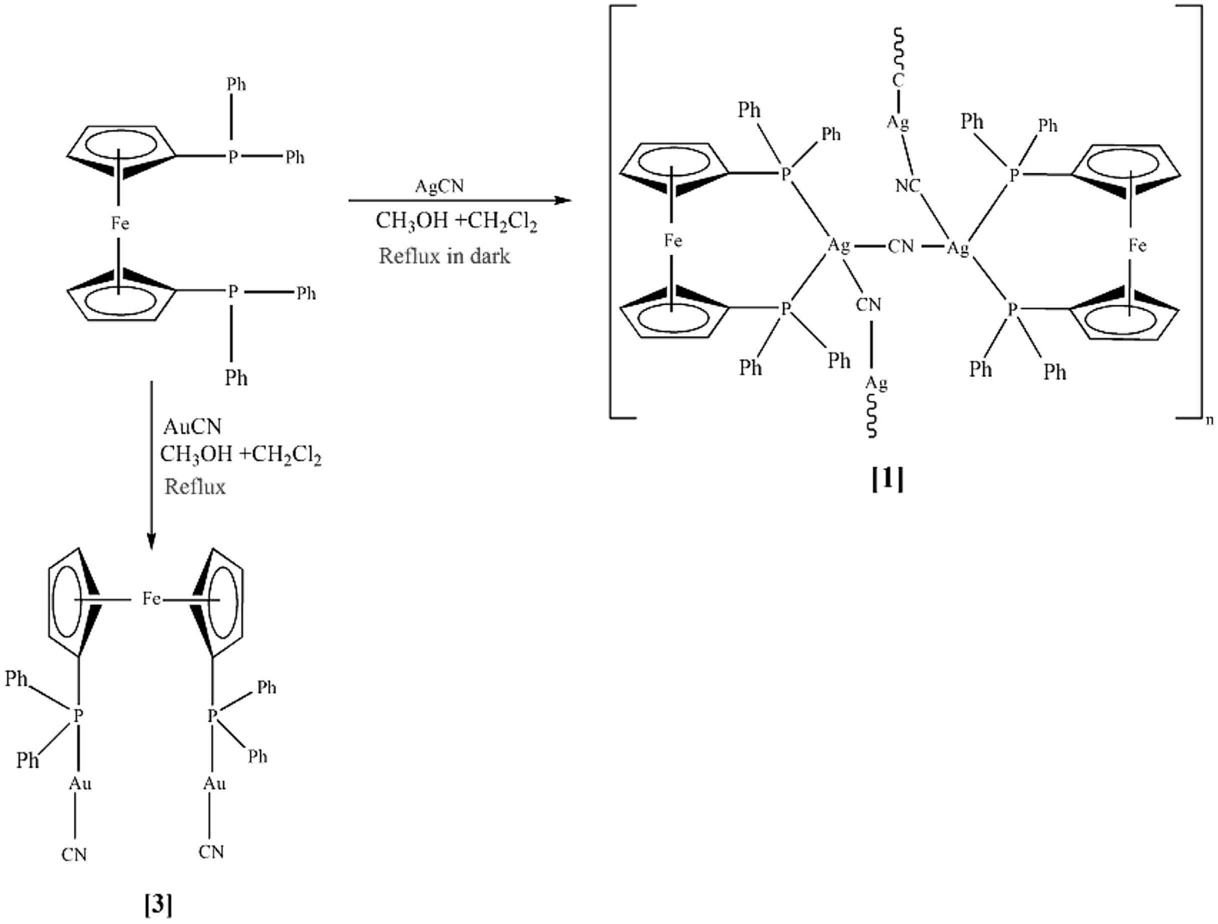
2. Results and discussion

2.1. Synthesis

The reactions of silver(I) cyanide with 1,1′-bis(diphenylphosphino)ferrocene (dppf)/1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf)/1,1′-bis(dicyclohexylphosphino) ferrocene (dcpf) ligand in a dichloromethane:methanol mixture (50:50 V/V) in equimolar ratio under refluxing with stirring in dark afforded the infinite one dimensional polymeric chains $[Ag_3(\mu_2\text{-}CN)_3(\kappa^2\text{-}P,P\text{-dppf})_2]_n\cdot C_6H_{12}$ (**1**), $[Ag_4(\mu_2\text{-}CN)_4(\kappa^1\text{-}P,P\text{-dtbpf})]_n$ (**2**) and centrosymmetric dimeric complex $[Ag_4(\mu_3\text{-}CN)_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dcpf})_2]$ (**5**), respectively (Schemes 1–3), while the reactions of gold(I) cyanide with dppf/dtbpf/dcpf under the similar condition mention above in presence of light led to the isolation of binuclear gold(I) complexes $[Au_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dppf})]$ (**3**), $[Au_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dtbpf})]$ (**4**) and $[Au_2(\mu_1\text{-}CN)_2(\kappa^1\text{-}P,P\text{-dcpf})]$ (**6**) (Schemes 1–3).

2.2. Characterization

All the complexes are air-stable, non-hygroscopic solids and soluble in dimethylformamide, dimethylsulfoxide and halogenated solvents but insoluble in petroleum ether and diethyl ether. The complexes were fully characterized by IR, UV–Vis, ^1H & ^{31}P NMR and ESI-MS. Analytical data of the complexes confirmed well to their respective formulations. More information about composition of the complexes was also obtained from ESI-MS. The positions of different peaks and overall fragmentation patterns in the ESI-MS of the respective complexes are consistent with their formulations. Infrared spectra of all the complexes exhibited characteristic band corresponding to $\nu_{C\equiv N}$ at 2136 cm^{-1}, 2114 cm^{-1}, 2138 cm^{-1}, 2151 cm^{-1}, 2129 cm^{-1} and 2147 cm^{-1}, respectively. However, only one $\nu_{C\equiv N}$ band agrees well with the presence of only one type of cyanide bridge between silver and gold (I) atom [58–62] which is in accordance with those reported in literature for bridging pseudohalide groups [30,56–60]. The ^1H NMR spectra of all the complexes show two singlets in the range of $\delta = 4.43–4.10$ ppm corresponding to $\eta^5\text{-}C_5H_4$ protons of the dppf, dtbpf and dcpf ligand. The phenyl ring protons of dppf ligand in complex **1** and **3** resonated as a multiplets at $\delta = 8.10–7.30$ ppm. The *tert*-butyl protons in complex **2** and **4** were observed as two overlapping doublets at $\delta = 1.21$ ppm. The cyclohexyl proton in complex **5** and **6** were observed as multiplet at 2.71–1.22 ppm. The $^{31}P\{^1H\}$ NMR spectra for the complex **1**, **2**, and **5** resonated at δ −2.559 (**1**), 41.54 (**2**), and 56.6 (**5**) as a broad singlets, while the other complexes **3**, **4**, and **6** showed a single sharp resonance at δ 31.4 (**3**), 64.9 (**4**), and 41.6 ppm (**6**), respectively for dppf, dtbpf and dcpf ligands indicating that all the phosphorus atoms were chemically equivalent (See **F-1**–**F-3**, Supporting material). These chemical shifts are within the accepted range and are comparable to that of the silver(I) and gold(I) complexes containing dppf, dtbpf and dcpf ligands [27,28,30,32,33,35,37–43,61]. All the complexes exhibited two bands at 460–478 nm and 265–266 nm in dichloromethane solution (See **F-4**, Supporting material). The lower-energy band in the range of 460–478 nm can be assigned to the d–d transition



Scheme 1. Synthetic Routes for **1** and **3**.