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Silver(I) ferrocenylcarboxylate: Reactivity and reaction behavior toward phosphines and phosphites

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ABSTRACT

Silver(I) ferrocenylcarboxylate $[Fe(\eta^5\text{-}C_5H_4CO_2Ag)(\eta^5\text{-}C_5H_5)]$ (**1**) subsequently decarboxylates either in boiling dichloromethane or tetrahydrofuran to give biferrocene $[Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)]_2$ (**2**) and elemental silver. Phosphine silver(I) ferrocenylcarboxylates of type $[Fe(\eta^5\text{-}C_5H_4CO_2Ag(PR_3)_n)(\eta^5\text{-}C_5H_5)]$ (R = Ph: **4a**, $n = 1$; **4b**, $n = 2$; **4c**, $n = 3$. R = *n*-Bu: **5a**, $n = 1$; **5b**, $n = 2$; **5c**, $n = 3$. R = OMe: **6a**, $n = 1$; **6b**, $n = 2$; **6c**, $n = 3$) are accessible by treatment of **1** with PR_3 (**3a**, R = Ph; **3b**, R = *n*-Bu; **3c**, R = OMe) in the ratio of 1:n. With dppe (**7**) tetrametallic $[Fe(\eta^5\text{-}C_5H_4CO_2Ag(\mu\text{-dppe}))(\eta^5\text{-}C_5H_5)]_2$ (**8**) (dppe = $Ph_2PCH_2CH_2PPh_2$) was formed. The structures of **4b** and **8** in the solid state have been determined by single X-ray structure determination. In **4b** the silver(I) ion possesses a pseudo-tetrahedral environment, whereby the four coordination sites are occupied by the chelated $FcCO_2$ unit and two datively-bonded PPh_3 ligands. Compound **8** forms in the solid state a dimer setup by a $[Ag(\mu\text{-dppe})]_2$ central building block. The $FcCO_2$ groups are chelated to Ag(I) thus resulting in a pseudo-tetrahedral coordination sphere at silver. The solution behavior of **4**–**6** was analyzed by temperature-dependent $^{31}P\{^1H\}$ NMR studies indicating ligand exchange processes.

1. Introduction

Ferrocenecarboxylic acid is known since quite some time and its reactivity and reaction chemistry, respectively, has been viewed in terms of cluster synthesis [1,2], surface modification and bioinorganic applications including biosensors [3], and, for example, catalysis [4], since the ferrocene backbone is a brilliant building block for the construction of new molecules and materials with tailor-made properties, due to its robustness, well-established synthesis methodologies, and excellent redox properties. On the other hand, silver(I) carboxylates of type $[AgO_2CR]$ and $[AgO_2CR(L_n)]$, respectively, (R = single-bonded organic ligand) gained recently interest because they can be used as precursors in, for example, metallization processes using Chemical Vapor Deposition (CVD), Atomic Layer Deposition (ALD) [5,6], spin-coating [7], inkjet printing [8] or combustion-CVD [9] techniques to obtain silver films as well as patterns on different substrate materials. In addition, they are of importance as building blocks in the preparation of hetero(multi)nuclear transition metal complexes [10]. However, only less is known about their structural features both in solution and in the solid state. Very recently, the use of 1′-(diphenylphosphanyl)-1-ferrocenecarboxylic acid (Hdpf) in the synthesis of silver(I)-based heterooligometallic complexes was reported, because the appropriate coordination sites within these species allowed to prepare complexes of higher nuclearity [11]

With this in mind and as a continuation of our research in the field of synthesizing (hetero)multimetallic complexes using ferrocene derivatives as structural building block motifs [10], we here describe the physical and chemical behavior of the silver(I) ferrocenylcarboxylate $[Fe(\eta^5\text{-}C_5H_4CO_2Ag)(\eta^5\text{-}C_5H_5)]$. The solid-state structure of two samples is reported as well.

2. Results and discussion

The thermal behavior of the silver(I) ferrocenylcarboxylate $[Fe(\eta^5\text{-}C_5H_4CO_2Ag)(\eta^5\text{-}C_5H_5)]$ (**1**), accessible by the reaction of $Fe(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_5)$ with $[AgNO_3]$ in presence of NEt_3 [10a], was studied. Therefore, **1** was suspended in either dichloromethane or tetrahydrofuran and the corresponding reaction mixture was heated to reflux. It was observed that in the higher boiling solvent the decomposition occurred more rapidly, as expected (Experimental Part). Upon thermolysis, a brownish slurry was formed, whereby silver precipitated in form of a silver mirror on the Schlenk

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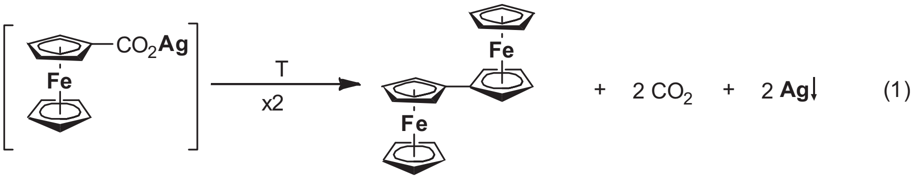


1

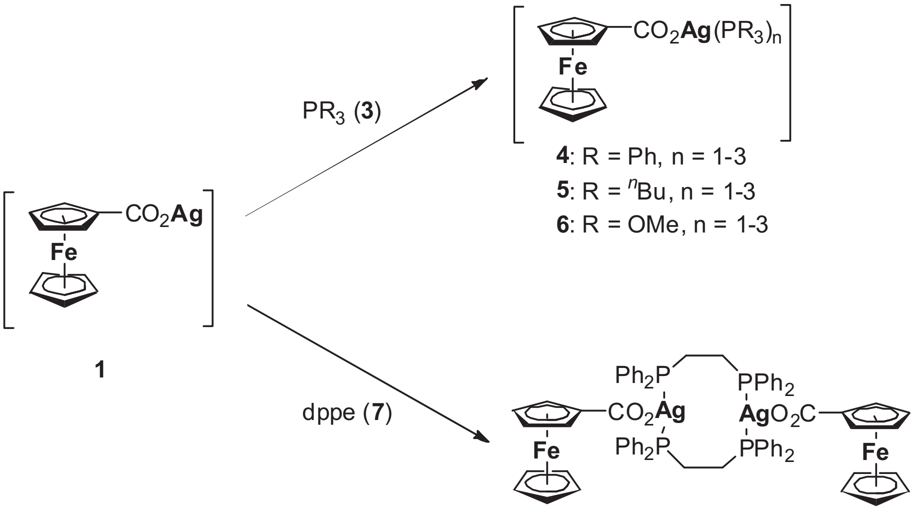
Scheme 1.

tube walls. From the slurry, orange biferrocene (**2**) could be isolated by subsequent crystallization. The release of CO_2 was proven by passing the gaseous components through a barium hydroxide solution, whereby precipitation of barium carbonate was observed. The isolation of **2** together with elemental Ag shows that **1** decomposes in a consecutive process including decarboxylation as well as homolytic bond cleavage and bond coupling reactions. In summary, this thermal behavior enriches the synthesis methodologies for preparing biferrocene [12]. In general, the thermal decomposition of silver(I) carboxylates of formula $[AgO_2CR]$ (R = organic ligand) to afford R_2 was studied by Fields and Meyerson [13]

It is established that *non*-soluble coordination oligomers and polymers can be converted to, for example, lower aggregated or even mononuclear species upon addition of 2- or 4-electron Lewis-base molecules including phosphines, phosphites, amines or sulfanes. Thus, we reacted **1** with PR_3 (**3a**, R = Ph; **3b**, R = *n*-Bu; **3c**, R = OMe) in the ratio of 1:n (n = 1, 2, 3) and with dppe (**7**) (diphenylphosphinoethane), respectively, in tetrahydrofuran as solvent at ambient temperature. Within these reactions the ferrocenylcarboxylato silver(I) phosphines $[Fe(\eta^5\text{-}C_5H_4CO_2Ag(PR_3)_n)(\eta^5\text{-}C_5H_5)]$ (R = Ph: **4a**, $n = 1$; **4b**, $n = 2$; **4c**, $n = 3$. R = *n*-Bu: **5a**, $n = 1$; **5b**, $n = 2$;**5c**, $n = 3$. R = OMe: **6a**, $n = 1$; **6b**, $n = 2$; **6c**, $n = 3$) and tetrametallic $[Fe(\eta^5\text{-}C_5H_4CO_2Ag(\mu\text{-dppe}))(\eta^5\text{-}C_5H_5)]_2$ (**8**) were formed in yields between 90 and 95% (Experimental Part) (Schemes 1 and 2). Within all of these reactions soluble species were formed which, after appropriate work-up, could be isolated as pale yellow to orange colored solids (**4a**, **4b**, **8**), waxy materials (**5a**) or liquids (**4c**, **5b**, **5c**, **6a**–**c**). It is obvious that the more Lewis-base ligands are available at silver(I), the more stable the organometallic complexes against air and moisture are. Better solubility of the corresponding complexes can be achieved by increasing the number of Lewis-bases at silver(I). For example, complexes possessing three phosphine or phosphite ligands, respectively, or featuring the dppe chelating moiety, can safely be handled for a short period of time in air without significant decomposition or oxidation of the appropriate phosphines or phosphites. However, it must be emphasized that **4**–**6** and **8** should best be stored in the dark and that all chemical manipulations should be performed with exclusion of light, otherwise decomposition upon formation of elemental silver is observed. Concerning the overall stability of **4**–**6** following trend can be seen **4** > **5** > **6**, whereby complexes **4a**–**c** are the most stabile species.

The identity of **4**–**6** and **8** has been confirmed by elemental analysis as well as IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy. The molecular structures of **4b** and **8** in the solid state were additionally determined by single X-ray structure analysis, thus confirming the structural assignments made from spectroscopic analysis.

Most characteristic in the IR spectra of **4**–**6** and **8** are their ν_{CO2} vibrations (Experimental Part). The strong ν_{CO2} absorptions of the carboxylato units are observed between 1330 and 1460 ($\nu_s(CO_2)$) and 1540–1590 cm^{-1} ($\nu_a(CO_2)$) (ν_s = symmetric, ν_a = *anti*-symmetric O–C–O stretching mode), which is typical in transition metal chemistry [14]. Whereas the *anti*-symmetric $\nu(CO_2)$ bands can always be detected, the respective symmetric vibrations only at times, which is attributed to additional ligand absorptions in this region, *i.e.* for the respective phosphite derivatives only ν_a could be observed. The $\Delta\nu$ value ($\Delta\nu = \nu_a - \nu_s$) gives a first hint if the carboxylic anions bind in a mono-, bi-dentate or chelating fashion



1

8

Scheme 2. Synthesis of **4**–**6** and **8** by phosphine or phosphite treatment of **1**.