Journal of Organometallic Chemistry, 81 (1974) 111–114

THE NICKEL-CATALYSED CARBONYLATION OF 2-MERCAPTOETHANOL

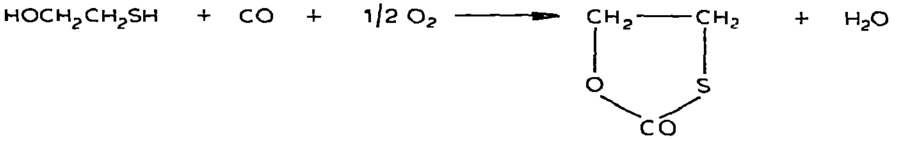
PAOLO KOCH and EMILIO PERROTTI
SNAM Progetti DIRIS, 20097 S Donato Milanese, Milano (Italy)
(Received May 13th, 1974)

Summary

2-Mercaptoethanol undergoes carbonylation in pyridine solution in the presence of oxygen and of [$Ni(CO)_3Py$] as a catalyst to give cyclic *O,S*-ethylenethiocarbonate. The isolation of thiolato–nickel compound [$Ni(SCH_2CH_2OH)_2$] by the oxidation of a solution containing [$Ni(CO)_3Py$] and 2-mercaptoethanol, and its reaction with carbon monoxide to give the cyclic thiocarbonate and [$Ni(CO)_3Py$] prove that the reaction proceeds in at least two steps.

Introduction

Evidence for carbon monoxide insertion into a metal–nitrogen bond [1] and a metal–oxygen bond [2] has been put forward to explain the metal catalysis of the carbonylation of amines to ureas and of alcohols to carbonates Although a considerable body of literature deals with metal–thiolato compounds, no published data exist on the reaction of these complexes with carbon monoxide to give thiocarbonates. We describe here the synthesis of cyclic *O,S*-ethylenethiocarbonate from 2-mercaptoethanol, carbon monoxide and oxygen using $Ni(CO)_4$ as a catalyst (eqn. 1). In order to understand the course of this reaction,



(1)

we have sought evidence for reaction intermediates and, under experimental conditions similar to the catalyzed synthesis, have isolated a bis(2-mercaptoethanol)-nickel(II) compound [$Ni(SCH_2CH_2OH)_2$] and investigated the reaction of this complex with carbon monoxide.

Results and discussion

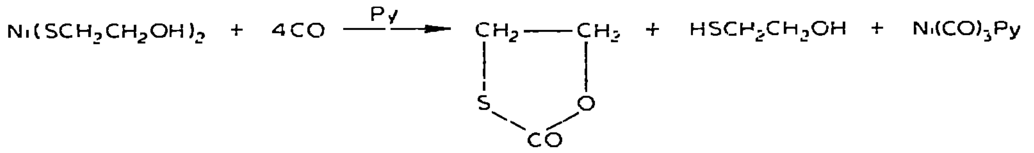
A mixture of $Ni(CO)_4$ and pyridine evolves carbon monoxide and produces a yellow solution containing $[Ni(CO)_3Py]$ [3]. When 2-mercaptoethanol is added to this solution and air bubbled through, a brown precipitate is formed (eqn. 2).

$$Ni(CO)_3Py + 2HSCH_2CH_2OH + 1/2\ O_2 \rightarrow Ni(SCH_2CH_2OH)_2 + 3CO + H_2O \quad (2)$$

This compound is insoluble in water and in most organic solvents, which is in accord with a linear polymeric structure[*] in which the nickel atoms are joined to each other by doubly-bridging mercapto groups [6]

The air oxidation of thiols to disulphides in the presence of basic catalysts [7] and the oxidative addition of organic disulphides to nickel(0) complexes [8] are two well-known reactions which might account for the formation of $[Ni(SCH_2CH_2OH)_2]$ in eqn. 2 However, failure of $[Ni(CO)_3Py]$ to react with bis(2-hydroxy ethyl) disulphide, under the experimental conditions in which reaction 2 is readily accomplished, rules out the hypothesis that the actual reacting species is the disulphide.

The complex formed in reaction 2 does not react with carbon monoxide when suspended in poor donor solvents, but in pyridine it is carbonylated at 60° with carbon monoxide at 3 atm Cyclic *O,S*-ethylenethiocarbonate is formed in 90% yield based on Ni. The infrared spectrum of the light yellow final pyridine solution shows bands at 2038, 2066 and 1973 cm^{-1} which have been attributed to $\nu(CO)$ of $[Ni(CO)_3Py]$ [3]. The stoichiometry of carbon monoxide absorption, may be accounted for as in eqn 3. The carbonylation of 2-mercaptoethanol in the presence of $Ni(CO)_4$ as a catalyst is carried out in pyridine at 60° using a mixture of carbon monoxide and oxygen (10/2 vol/vol) at 3 atm. Cyclic *O,S*-ethylenethiocarbonate is formed in 60% yield. Bis(2-hydroxyethyl) disulphide is a by-product of the reaction, and it becomes the main product when CO/O_2 mixtures containing more oxygen than 10/2 vol/vol are employed. The infrared spectrum of the final pyridine solution shows bands characteristic of $[Ni(CO)_3Py]$. In the light of the results reported this carbonylation can be formulated as the sum of reactions 2 and 3 where $[Ni(CO)_3Py]$ is the active catalyst



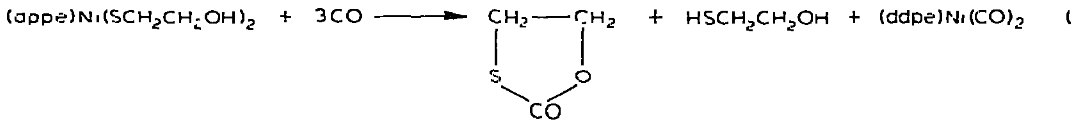
(3)

In the hope of obtaining a system more efficient than the one employing pyridine as solvent, we have studied the carbonylation of a thiolato—nickel complex with a chelating phosphine ligand $[Ph_2PCH_2CH_2PPh_2Ni(SCH_2CH_2OH)_2]$ in poorly-coordinating solvents. This red diamagnetic complex is very soluble in chloroform or dichloromethane and slightly soluble in ethanol. Molecular weight determinations in 1,2-dichloroethane solution agree with the monomeric formula (found 590, calcd 611.7). On this basis a four-coordinated square structure is proposed

---

[*] Soluble hexameric thiolato—nickel compounds with a ring structure were also reported [4, 5]

This complex readily reacts with carbon monoxide, when dissolved in 1,2-dichloroethane or suspended in ethanol, according to eqn. 4 We tentatively



(4)

suggest that this carbonylation may require the initial coordination of carbon monoxide to the thiolato–nickel complex, followed by insertion into the nickel–sulphur bond to give an intermediate carbothiolatonickel(II) species [Ni—CO—SCH_2CH_2OH] which undergoes a free-energy favoured ring closure to the cyclic thiocarbonate.

Experimental

All solvents were dried and stored under nitrogen. 2-Mercaptoethanol was fractionated under reduced pressure before use. Cyclic *O,S*-ethylenethiocarbonate was identified by comparison of its infrared and mass spectra and GLC retention time with those of authentic samples. Quantitative analysis for the thiocarbonate was made by infrared spectroscopy using the band at 1740 cm^{-1} and standard samples for calibration.

[Ni(SCH₂CH₂OH)₂]

Air was slowly bubbled through a solution of $Ni(CO)_4$ (14 5 × 10^{-3} mol) and 2-mercaptoethanol (37.2 × 10^{-3} mol) in pyridine (50 ml) at room temperature. The solution was filtered, the precipitate washed with ethanol, and dried in vacuo. Yield 2.68 g (86% based on Ni). (Found C, 22 1 H, 4 9, Ni, 26 8; S, 29.3. $C_4H_{10}NiO_2S_2$ calcd.. C, 22.6; H, 4.7; Ni, 27 6, S, 30.1%)

[Ph₂PCH₂CH₂PPh₂Ni(SCH₂CH₂OH)₂]

To a suspension of [(dppe)$NiCl_2$] [9] (5.5 × 10^{-3} mol) in ethanol (50 ml) was added a solution of $LiSCH_2CH_2OH$ (13 mol) in ethanol (10 ml), and the mixture was stirred for one hour. The red solid was filtered off, washed with ethanol and dried in vacuo. Yield 3.2 g (95% based on Ni). (Found: C, 58.1; H, 5.7; Ni, 9.1; S, 10.7. $C_{30}H_{34}NiO_2P_2S_2$ calcd.: C, 58.9, H, 5.5; Ni, 9.6; S, 10.5%.)

Carbonylation experiments

(a). A suspension containing [$Ni(SCH_2CH_2OH)_2$] (1.93 × 10^{-3} mol) in pyridine (20 ml) was heated at 60° with carbon monoxide at 3 atm pressure. After 6 h the solid had dissolved and 7.6 × 10^{-3} mol of gas were absorbed. The resulting solution was analyzed by infrared for ethylenethiocarbonate. Yield 1.8 × 10^{-3} mol (93% based on Ni).

(b) A solution of [(dppe)$Ni(SCH_2CH_2OH)_2$] (2.2 × 10^{-3} mol) in 1,2-dichloroethane (50 ml) was treated for one hour at 25° with carbon monoxide at 3 atm pressure. The solution was distilled at reduced pressure while cooling the receiver at —78°. The residue of the distillation was extracted with benzene to

give [(dppe)Ni(CO)$_2$] [10] (2.0 × 10^{-3} mol). The distillate was analyzed by GLC for 2-mercaptoethanol (1.8 × 10^{-3} mol) and ethylenethiocarbonate (1.9 × 10^{-3} mol). Yield 82% based on Ni.

(c). A solution of Ni(CO)$_4$ (2.3 × 10^{-3} mol) and 2-mercaptoethanol (28.6 × 10^{-3} mol) in pyridine (25 ml) was heated at 80° under 3 atm of a CO/O$_2$ mixture (10/2 vol/vol). After 10 h the gas absorption had stopped and the solution was analyzed for ethylenethiocarbonate. Yield 17.3 × 10^{-3} mol (60% based on 2-mercaptoethanol).

References

1 J P. Candlin, K A Taylor and D T Thompson, Reactions of Transition Metal Complexes, Elsevier, Amsterdam, 1968, p. 135
2 T Sagusa, T. Tsuda and K Isayma, J Org Chem , 35 (1970) 2976
3 W. Hieber, J. Elleman and E Zhan, Z Naturforsch B, 18 (1963) 589
4 R O. Gould and M M Harding J Chem Soc A, (1970) 875
5 P Woodward, L F Dhal, E W Abel and B C Crosse, J Amer Chem Soc , 87 (1963) 5251,
6 K A Jensen, Z Anorg Allg. Chem 252 (1944) 227
7 A. A. Oswald and T.J. Wallace, in N Kharasch and C.Y Meyers (Ed), The Chemistry of Organic Sulfur Compounds, Vol. 2, Pergamon Press, Oxford, 1966, p 205
8 R G Hayter and F S Humiec, J Inorg Nucl Chem , 26 (1964) 807
9 G Booth and J Chatt J Chem Soc , (1965) 3238
10 J Chatt and F A Hart, J Chem Soc , (1960) 1378.