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Journal of Organometallic Chemistry 691 (2006) 3715–3717

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Communication

A oxygen-dependent reductive dechlorination of chloroform by (Bisdiphenylphosphinomethane)cobalthexacarbonyl $Co_2(CO)_6(dppm)$

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Received 19 May 2006; received in revised form 31 May 2006; accepted 31 May 2006
Available online 10 June 2006

Abstract

The reaction of $Co_2(\mu\text{-dppm})(CO)_6$ with aerated chloroform affords $[Co\{Ph_2P(O)CH_2P(O)Ph_2\}_3][CoCl_4]$ in low yield, and this reaction is demonstrated to be prevented under anaerobic conditions representing an unusual example of a reductive dechlorination which only takes place in the presence of oxygen.

Keywords: Dehalogenation; Dechlorination; Cobalt carbonyl; Dicobalthexacarbonyl; Phosphines

Dicobalthexacarbonyl alkyne complexes are of interest as they are intermediates in important carbon–carbon bond-forming reactions [1], and they are of significance in the area of molecular electronics [2]. These complexes can be stabilised by the use of bridging diphosphine ligands, and in particular there are many examples of dicobalthexacarbonyl alkyne complexes which are bridged by bis(diphenylphosphino)methane (dppm) [3]. These are usually prepared by the reaction of the bridged dicobalt hexacarbonyl complex $Co_2(\mu\text{-dppm})(CO)_6$ **1** (Fig. 1) with the relevant alkyne under similar but more forcing conditions to those employed in the synthesis of the non-bridged species (e.g. small excess of cobalt species, benzene solution at reflux). While it is known [4] that dicobalt octacarbonyl reacts with chloroform, to give the tetrahedral cluster $CH(Co(CO)_3)_3$, the derived alkyne complexes are typically unreactive to chloroform, and we have thus routinely recorded NMR spectra in $CDCl_3$ (see Fig. 2).

Equally, while dicobalt octacarbonyl is (slowly) oxidised in air, the derived alkyne complexes when phosphine bridged are, typically, air-stable, or at least significantly more stable, and thus it is generally unnecessary to use Schlenk techniques when handling these complexes. We have, however, noted an unusual reaction between $Co_2(\mu\text{-dppm})(CO)_6$ and aerated $CDCl_3$. When a solution of a reaction mixture containing $Co_2(\mu\text{-dppm})(CO)_6$ in $CDCl_3$ was left for 2 weeks the growth of a deposit of a fine microcrystalline green powder was observed. As there was no evidence of the degradation of the desired product this deposit was assumed to be derived from the (slight) excess cobalt starting material, $Co_2(\mu\text{-dppm})(CO)_6$. The colour and lack of chloroform-solubility of this by-product suggested that it was an oxidation product; however, this is not the product we have previously observed upon aging of **1** which is typically the expanded cluster $Co_4(\mu\text{-dppm})_2(CO)_8$ which has been previously characterised [5]. Thus, samples of $Co_2(\mu\text{-dppm})(CO)_6$ were exposed to air both neat and in a variety of solvents. The characteristic green powder was observed only when $Co_2(\mu\text{-dppm})(CO)_6$ was exposed to air in chloroform: in other solvents degradation was much slower and gave intractable brown solid and colourless crystals of the bis phosphine oxide derived from dppm (dppmdo) [6]. Eventually a crystal of the char-

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doi:10.1016/j.jorganchem.2006.05.053

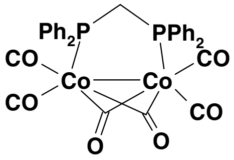

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Fig. 1. Molecular structure of **1**.

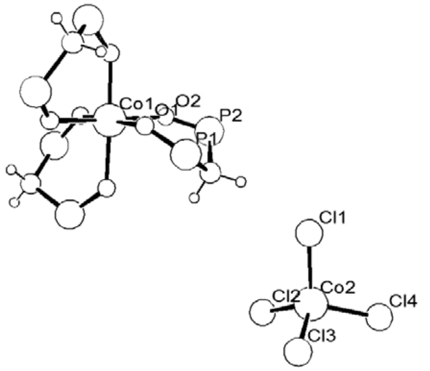
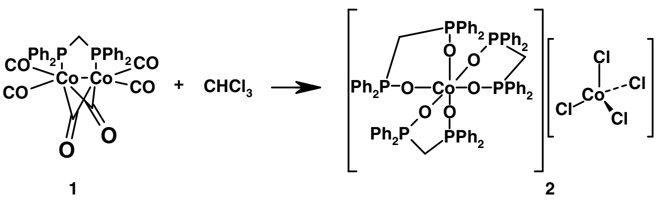


Fig. 2. ORTEP [10] view of **2** (50% probabilities) phenyl rings omitted for clarity.

acteristic green product was obtained which was suitable for single crystal X-ray diffraction studies [7], and the structure was determined to be an electrolyte consisting of a cationic cobalt complex with a single Co^{2+} ion with octahedral geometry chelated by three dppmdo ligands, $[Co(dppmdo)_3]^{2+}$ and a cobalt (II) tetrachloride $[CoCl_4]^{2-}$ counterion (along with several chloroform molecules of crystallisation). This product has been previously reported from the reaction of dppmdo with cobalt chloride but has not been structurally characterised [8]. The formation of this product was entirely unexpected and there is great interest in dechlorination of organic species as they make up an important family of toxic, long-lived pollutants [9]. Therefore, both the academic interest and possible utility of a derived process led to an investigation of this reaction (see Scheme 1).

As it is known that low valent cobalt species will dechlorinate chloroform [4] it was initially assumed that the product had been formed in two steps, firstly, the reductive dechlorination of chloroform by electron transfer from the low valent Co starting material to form oxidised cobalt and chloride, followed by aerobic oxidation of free dppm to the dioxide, all of which subsequently crystallised as the salt **2**. In an attempt to observe the initial product the reaction was monitored by ^{31}P NMR. By this technique both the loss of the $Co_2(\mu\text{-dppm})(CO)_6$ (δ_P 59) and the formation of the dppmdo complex **2** (δ_P121) can be observed and reaction was studied under a variety of different conditions. In fact, it was found that in thoroughly degassed chloroform $Co_2(\mu\text{-dppm})(CO)_6$ is stable (at ambient temperature) for periods of up to a month. Therefore, it seems that the formation of **2** requires oxygen, not only for the phosphine oxide formation, but for the dechlorination of chloroform, as this would be observed as a loss of **1** in the ^{31}P NMR. As the final product **2** slowly precipitates the ratio of ^{31}P signals for **1** and **2** were not relied on to confirm the progress of reaction, and an internal standard (Ph_3PO) was used to allow accurate monitoring of the loss of **1**. It is also worth noting that no sign of the monooxide of dppm (δ_P-27, +29, J_{PP} 50 Hz) [11] is observed in the reaction mixture. The mono-oxide is the major product in the aerobic oxidation of dppm in the absence of Co, implicating Co catalysis in the oxidation. In fact, the disappearance of the starting material signal and the appearance of the product signal are not accompanied by any signals which could be attributed to intermediate materials such as unbound dppm, new intermediate complexes or the monooxide. Clearly the failure to observe an entity is not proof of it non-existence but there must never be any appreciable concentration of any of these species in solution. It was further noted that allowing a small quantity of air into the system produces a small degree of reaction, which then stops until further air is allowed in. This finding discounts any radical-chain type mechanism for the dechlorination which could be triggered by dioxygen, as no continuing loss of **1** is observed under these conditions.



Scheme 1.

It is worth noting that the stoichiometry of the reaction requires by-products containing hydrocarbon and cobalt, as the dppm to Co ratio is greater in **2** than **1** and the dechlorination of chloroform leaves CH fragments. Unfortunately efforts to determine the composition of the byproducts are hampered by their intractable nature, and by contamination with **2**.

Given the difficulties in characterising the other products, at present all that can be stated with certainty regarding the mechanism of reaction is that the starting materials are stable in the absence of oxygen, implicating a limiting initial aerobic oxidation of **1** (possibly involving loss of a carbonyl). It is possible that a reactive species produced from this oxidation then dechlorinates chloroform and is thus oxidised to the Co^{II} product. Given the lack of observation of free dppm or dppm monooxide it is likely that a Co-oxygen species then oxidises dppm, and, as dppm and the monooxide are never observed these two oxidations must be extremely rapid (faster than the disappearance of **1**) and it seems likely therefore that these reactions are intramolecular, i.e. involve coordinated dppm.

In conclusion the oxygen-dependence of the reaction between chloroform and **1** has been demonstrated. Further

Table 1
Crystal data for **2**

Crystal data and experimental details for **2**, green block, stable under ambient conditions collected on a Nonius KappaCCD solved using direct methods [7]

Formula	$C_{83}H_{74}Cl_{28}Co_2O_6P_6$
M	2463.70
Temperature (K)	150
Crystal system	Cubic
Space group	$P213$
λ (Å)	0.71073
Unit cell dimensions	
a (Å)	21.8970(3)
b (Å)	21.8970(3)
c (Å)	21.8970(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	10499.1(2)
Z	4
Absorption coefficient (mm^{-1})	1.168
Crystal size (mm^3)	$0.30 \times 0.40 \times 0.48$
θ limits (°)	3.84 26.37
Reflections collected	71743
Unique observed reflections [$F_o > 4\sigma F_o$]	7172
R(int)	0.1297
Goodness-of-fit on F^2	1.089
Final R indices, [$I > 2\sigma(I)$]	
R_1	0.0780
$wR_2(F)^2$	0.1787
(all data)	
R_1	0.0919
$wR_2(F)^2$	0.1872
Flack parameter	0.0199 (0.0350)

studies will attempt to fully explore the mechanism of the reaction and to probe the possibility of developing a catalytic version which may be of use in the dechlorination of pollutants.

We are grateful to the EPSRC Mass Spectrometry unit (Swansea) for assistance and the EPSRC for support (GR/S11480/01 Meritxell Casadesus, EP/COO7255 Sarah Oakley).

1. Experimental

[Co(dppmdo)$_3$][CoCl$_4$] **2** (see Table 1).

$Co_2(CO)_6$dppm (20 mg, 0.0275 mmol) was dissolved in $CHCl_3$(1 mL) and the solution was left open to the air for 5 days. The solid formed was collected by filtration, washed with chloroform and dried to give **2** (16%) as green blocks m.p.: 212 °C ^{31}P (121 MHz, CDCl3): δ 25.4 ppm; dH (400 MHz, d6 DMSO) 7.75 (s, br, 2H) 7.40 (s, br, 3H) 4.10 (s, br, 1H) ν_{max} 1153.9, 1123.6 cm^{-1}. M/Z. ES+ theoretical isotope pattern for [Co(dppmdo)$_3$]$^{2+}$ 653.6 100% 654.1 85% 654.6 40%. Observed: 653.8 98% 654.3 100% 654.8 45%. (MALDI): Theoretical isotope pattern for [(dppmdo)$_2$CoCl]$^+$: 926.1(100%); 927.1(56%); 928.1(47%); 929.1(20%); 930.1(5%). Observed: 926.1(100%); 927.1(70%); 928.1(54%); 929.1(17%); 930.1(5%). $C_{75}H_{66}Cl_4Co_2O_6P_6$.1.5 $CHCl_3$ requires C 54.4 H 4.03 found C 54.18 H 4.22%.

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallography Data Centre, CCDC 607980 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.053.

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