Journal of Organometallic Chemistry, 384 (1990) 217–221
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20431

The reaction of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ with iodine and mercuric halides

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(Received August 21st, 1989)

Abstract

The reaction of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ with iodine gives two insoluble products which are formulated as $[\{Co_2I(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)\}_2CH_2\}_n][I]_n$ and $\{\text{-}I\text{-}Co(I)(\eta^5\text{-}C_5H_4CH_2C_5H_4\text{-}\eta^5)Co(I)\}_n$ with a few $(C_5H_4)Co(CO)I_2$ end-groups, and two soluble but not isolable products which are formulated as $[\{Co(CO)I_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ and $[Co(CO)_2(\eta^5\text{-}C_5H_4CH_2C_5H_4\text{-}\eta^5)Co(CO)(I)_2]$ on the basis of their infrared spectra. The reactions of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ with mercuric halides give insoluble 1/1 adducts containing Co–Hg bonds in a reaction which is reversed by addition of donor solvents such as acetonitrile or by compressing the adducts in alkali metal halide discs.

Introduction

The cobalt atom in $[Co(\eta\text{-}C_5H_5)(CO)_2]$ is basic. Reaction of this complex with electrophiles gives products such as $[(\eta\text{-}C_5H_5)(CO)_2CoHgX_2]$ [1,2] and $[(\eta\text{-}C_5H_5)(CO)_2CoHgX]X \cdot 2HgX_2$ [1,3] with Co–Hg donor–acceptor bonds. Consequently it seemed reasonable to expect that the presence of two cobalt atoms in $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ which could be close together would modify the reactivity of each (cf. ref. 4). For example, if one cobalt atom was subjected to electrophilic attack, the second could take part in the reaction either by forming a second electrophile–Co bond or a Co–Co bond to give products of types which are unlikely to be accessible from $[Co(\eta\text{-}C_5H_5)(CO)_2]$. This expectation has been realised in the reaction with iodine but not in those with mercuric halides.

Whilst this manuscript was in preparation it was reported that $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ reacts with iodine in ether to give $[\{Co(CO)I_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ [5], and that similar binuclear derivatives of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ in which the two cyclopentadienyl groups were linked directly or via a CH_2 bridge also reacted with oxidising agents to give diamagnetic cationic species containing a Rh–Rh bond [6]. Similar behaviour was observed for $[\eta^5,\eta^5\text{-}C_{10}H_8)\{Rh(CO)(PPh_3)\}_2]$, which is

0022-328X/90/$03.50

oxidised to the diamagnetic $[\mu\text{-}\eta^5,\eta^5\text{-}C_{10}H_8)\{Rh(CO)(PPh_3)\}_2]^{2+}$ dication [7], which also contains a Rh–Rh bond [8]. In all of these metal–metal bonded compounds the CO ligands are terminally bonded.

Experimental

The complex $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ was prepared as previously described [4]. Other chemicals were purchased and used as received.

All reactions were carried out in dried and deoxygenated solvents under nitrogen and at room temperature unless otherwise stated. Solvents were dried by refluxing over calcium hydride and distilled prior to use.

Infrared spectra were recorded on a Perkin Elmer 1710 FTIR spectrometer. Analyses were carried out in the Analytical Laboratory of University College, Dublin.

Reaction of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ with I_2

(i) A solution of iodine (0.13 g) in carbon tetrachloride or benzene (20 ml) was added slowly to one of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ (0.37 g; mole ratio 1/2) in the same solvent (25 ml). A brown solid separated, and was filtered off, washed with chloroform, and dried. The product could not be purified further (yield 80%). Its analysis was close to that for $[\{Co(CO)(I)(\eta^5\text{-}C_5H_4)\}_2CH_2]$. (Found: C, 28.9; H, 2.1; I, 45.7; Co, 19.5. $C_{13}H_{10}I_2Co_2O_2$ calcd.: C, 27.5; H, 1.8; I, 44.8; Co, 20.6%. IR spectra (KBr) ν(CO) 1847(w), 1886(s) cm^{-1} with very weak bands of variable intensity at 1953, 2020 and 2066 cm^{-1}. Similar results were obtained for reactions in a variety of other solvents.

(ii) A solution of iodine (0.52 g) in benzene or carbon tetrachloride (20 ml) was added slowly to one of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ (0.37 g; mole ratio 2/1) in the same solvent (25 ml). A brown solid separated, and was filtered off, washed with chloroform, and dried. Unfortunately, consistent analytical data could not be obtained for this compound. Spectroscopic data suggested that it is $[\{Co(CO)(I)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ (see below) but it always contained some solvent or other impurities, and it could not be purified since it decomposed in the solvents in which it dissolved.

Reaction of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ with HgX_2 (X = Cl, Br, I)

Mercury(II) halides were added to a solution of $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]$ (0.37 g) (mole ratio 1/1) in benzene (30 ml). Yellow solids precipitated immediately in 50–70% yield. They were filtered off, washed with chloroform and dried. Because of their insolubility they could not be purified further. All analysed as 1/1 adducts.

$[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]\cdot HgCl_2$. Found: C, 28.3; H, 1.4; Cl, 10.5. $C_{15}H_{10}Cl_2Co_2HgO_4$ calcd.: C, 27.9; H, 1.9; Cl, 10.9%. IR spectra (KBr) ν(CO): 2031, 2066 cm^{-1}.

$[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]\cdot HgBr_2$. Found C, 24.2; H, 1.4. $C_{15}H_{10}Br_2Co_2H_8O_4$ calcd.: C, 24.5; H, 1.6%. IR spectra (KBr) ν(CO): 2030, 2066 cm^{-1}.

$[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2]\cdot HgI_2$. Found: C, 21.1; H, 1.35; I, 29.55. $C_{15}H_{10}Co_2HgI_2O_4$ calcd.: C, 21.7; H, 1.45; I, 30.6%. IR spectra (KBr) ν(CO): 2023, 2063 cm^{-1}.

Results and discussion

Addition of a solution of iodine in benzene to one of [{Co(CO)$_2$(η^5-C$_5$H$_4$)}$_2$CH$_2$] (I) (mole ratio 1/2) at room temperature results in the partial consumption of I and an 80% yield of a black precipitate which analyses as [{Co(CO)(I)(η^5-C$_5$H$_4$)}$_2$CH$_2$] (II). If the reaction is carried out with increasing amounts of iodine, more of I is consumed, and the precipitated solid is shown by infrared spectroscopy to be a mixture of II with increasing amounts of a second product III. Similar results are obtained for reactions carried out in diethyl ether, carbon tetrachloride, chloroform or hexane.

If the reaction between I and iodine (mole ratio 1/2) is carried out at 0–5 °C, there is very little precipitate, and infrared spectroscopy shows that a single product (IV), for which ν(CO) 2070 cm^{-1}, is present in solution. If the solution is set aside, a black insoluble solid precipitates, and is found to be III contaminated with traces of II. When the reaction is carried out under an atmosphere of carbon monoxide, the soluble complex IV is the sole product, and remains in solution for many hours.

If the reaction in carbon tetrachloride is carried out with incremental addition of the iodine solution to that of I, ν(CO) 1964 and 2024 cm^{-1}, and is monitored by infrared spectroscopy, two soluble products can be detected. One is IV, ν(CO) = 2070 cm^{-1}, and the other is V with ν(CO) 1971, 2028 and 2058 cm^{-1}. This is always a minor product, which gives rise to weak absorption bands that are still present when those of I have disappeared, but they themselves disappear on the further addition of iodine. Absorption bands due to II could not be detected in the reaction solution at any stage.

Only II and III could be isolated as solids. V was always present only in small amounts, and removal of the solvent from solutions of IV resulted in its conversion to the insoluble III. Both II and III are black, air-stable solids, insoluble in all non-polar solvents, and soluble with decomposition in polar solvents such as acetonitrile or tetrahydrofuran (cf. [Co(η-C$_5$H$_5$)(CO)I$_2$] [9]). The infrared spectrum of II shows two absorption bands due to ν(CO) vibrations at 1847(s) and 1886(w) cm^{-1} (KBr disc, relative peak heights in parentheses), whose frequencies and relative intensities suggest that the molecule contains a near-planar Co(μ-CO)$_2$Co system similar to that in *cis*-[Fe(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)$_2$], to which it is structurally related but with both Fe(CO) replaced by CoI. A similar structural unit has been characterised crystallographically in [Co$_2$(η-C$_5$H$_5$)$_2$(μ-CO)$_2$(μ-GeCl$_2$Fe(CO)$_4$-Cl$_2$Ge)] [10] and [Co$_2$(η-C$_5$H$_4$Me)$_2$(μ-CO)$_2$(μ-*o*-xylylene)] [11] and identified spectroscopically in [Co$_2$(η^5,η^5-C$_5$H$_4$)(CH$_3$)$_2$(μ-CO)$_2$] [4], which has ν(CO) (THF solution) at 1830(s) and 1863(m) cm^{-1}. These ν(CO) frequencies are low compared with those for II as a consequence of the replacement of I by CH$_3$. The presence of μ-CO ligands in the Co complexes but not in the Rh [6,7] derivatives is as expected. The insolubility of II suggests that it is polymeric, perhaps a salt with cationic [Co$_2$(μ-CO)$_2$[μ-(η^5-C$_5$H$_4$)}$_2$CH$_2$}] moieties linked by Co–I–Co bridges as shown in Fig. 1, and iodide anions. Thus the hoped-for product has been obtained but its physical properties and instability in solution have prevented its further study.

The infrared spectrum of soluble IV is very similar to that of [Co(η-C$_5$H$_4$CH$_3$)(CO)I$_2$] (ν(CO) 2068 cm^{-1}). This suggests that it is [{Co(CO)I$_2$(η^5-C$_5$H$_4$)}$_2$CH$_2$], as isolated by Werner et al. [5], in which both cobalt atoms have been oxidised to Co$^{\text{III}}$. The polymeric III whose formation from IV may be slowed

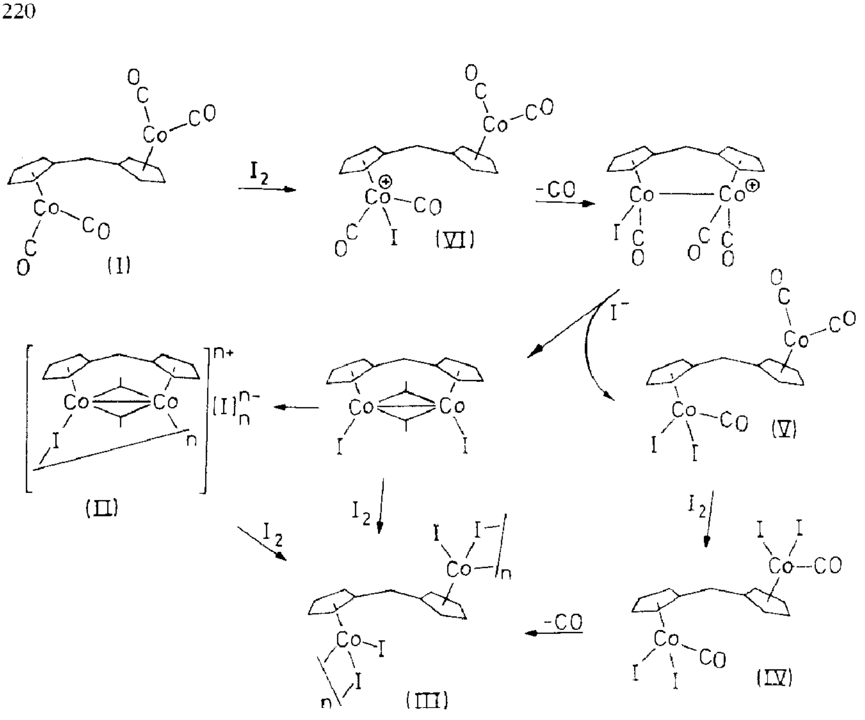

Fig. 1. Proposed pathway of the reaction between I and I_2. Bridging CO groups in II and its precursor are denoted by |.

by the presence of free carbon monoxide, is probably derived from IV by the loss of CO and the formation of polymers containing $\{-\text{I}-\text{Co(I)}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)(\text{Co(I)}\}_n$ chains with a few terminal Co(CO)I_2 groups which are responsible for the ν(CO) absorption band at 2066 cm^{-1}. This behaviour is similar to that of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{I}_2]$, which can be readily decarbonylated to give $[\text{Co}_2(\eta\text{-C}_5\text{H}_5)_2(\text{I})_2(\mu\text{-I})_2]$ [9].

The infrared spectrum of V is consistent with the structure $[\text{Co(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)\text{Co(CO)(I)}_2]$. The ν(CO) band at 2058 cm^{-1} is due to the Co(CO)I_2 moiety, whilst the bonds at 1971 and 2028 cm^{-1} are due to the Co(CO)_2 group. These frequencies are respectively lower and higher than those of IV (2070 cm^{-1}) and I (1964 and 2024 cm^{-1}) in carbon tetrachloride solution. This is attributable to the different substituents on the cyclopentadienyl ligands.

The initial product of the reaction of $[\text{Fe(CO)}_5]$ with Br_2 is $[\text{Fe(CO)}_5\text{Br}]\text{Br}$ [11]. The above observations may be rationalized if the reaction of I with I_2 proceeds by way of a similar species, $[\text{Co(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)\text{Co(CO)}_2(\text{I})]^+$ (VI), which has not been detected. As a consequence of the nucleophilicity of the Co(CO)_2 moiety (see below), VI could undergo an internal nucleophilic attack by this on the $\text{Co(CO)}_2\text{I}^+$ with displacement of CO and the formation of $[\text{Co}_2(\text{CO})_3(\text{I})\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2\}]^+$, contains a Co–Co bond. This may lose CO and polymerise to II or suffer nucleophilic attack by I^- at one cobalt atom or the other to give either $[\text{Co(CO)}_2(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{-}\eta^5)\text{Co(CO)I}_2]$ (V) or $[\{\text{Co(CO)(I)}\}_2(\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2\}]$, which subsequently polymerises to II. If the postulated intermediate VI were to undergo nucleophilic attack by I^- it would give V or $[\{\text{Co(CO)(I)}\}_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2\}]$, and hence II. The oxidation of either II or V would give IV, in reactions for which there is ample precedent.

Other electrophiles react with I to give products related to the above, but they are very unstable and could not be isolated.

However, mercury(II) halides convert I into insoluble orange 1/1 adducts which analyse as $[\{Co(CO)_2(\eta^5\text{-}C_5H_4)\}_2CH_2(HgX_2)]$. These are insoluble in most solvents except acetonitrile or tetrahydrofuran, in which they decompose to free I. The reversion of these adducts to I also takes place in alkali metal halide, MX, pressed discs. It increases in importance along the series $M = Cs > Rb > K > Na$ and $X = I > Br > Cl$, so that dissociation is complete in CsI discs but scarcely noticeable in NaCl. The ν(CO) vibrations of these adducts have much lower frequencies than those of the 3/1 adducts $[Co(\eta\text{-}C_5H_5)(CO)_2] \cdot 3HgCl_2$, 2069, 2092 cm^{-1} [1], and are close to but lower than those found for the 1/1 adducts $[Co(\eta\text{-}C_5H_5)(CO)_2] \cdot HgCl_2$, 2042 and 2074 cm^{-1} [1]. Hence we suggest that these adducts have polymeric structures of the type $[\{Co(CO)_2(\eta^5\text{-}C_5H_4CH_2C_5H_4\text{-}\eta^5)Co(CO)_2HgCl_2\}_n$ with two Co atoms coordinated to each mercury. The cobalt to mercury donor bonds are readily broken by Lewis bases such as halide ions or donor solvents.

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