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CHEMISTRY OF THE μ-HYDRIDOBIS(PENTACARBONYLCHROMIUM(0)) SPECIES

I. THE ADDITION REACTIONS OF ITS SALTS WITH N-DONOR BIDENTATE LIGANDS

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Summary

Reactions of the potassium and tetrabutylammonium derivatives of $Cr_2H(CO)_{10}^-$, with N-donor bidentate ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) have been investigated. A coordination compound of general formula $K[Cr_2H(CO)_{10}(phen)_3]$ is the most stable product from the reaction of the former with phen, but under certain conditions a 1/2 adduct may also be isolated. The analogous reaction with bpy leads to a single labile adduct, $K[Cr_2H(CO)_{10}(bpy)_2]$.

$(C_4H_9)_4N[Cr_2H(CO)_{10}(phen)]$ is formed by interaction of the latter derivative with phen, but bpy does not give the analogous adduct.

Introduction

In recent years more convenient preparations [1,2] of its sodium and tetraethylammonium derivatives have made the title metal carbonyl hydride (first isolated by Behrens et al. [3]) more accessible, and permitted structural investigations which have established the presence of an unusual linear electron-deficient Cr—H—Cr system [2,4,5]. Little is known about its chemical behaviour, even though species of this type are of interest in view of their potential catalytic activity and their use as reagents for the synthesis of organometallic derivatives. There has been an unsuccessful attempt at protonation [2], and addition of N-donor bidentate ligands such as ethylenediamine and 1,10-phenanthroline to aqueous solutions of the sodium salt is known to give bidentate $Cr(CO)_4$ complexes [6].

Because of its electron-deficient system, an acceptor—donor interaction between this anion and donor molecules might be expected. This would give rise to interesting structural possibilities. We have therefore examined the reaction of $Cr_2H(CO)_{10}^-$ with 1,10-phenanthroline (phen) more fully, and extended the study to reactions with the 2,2'-bipyridine (bpy) ligand, using the potassium and tetrabutylammonium derivatives obtained by a very convenient route described in this work. These reactions gave new coordination compounds rather than the reported bidentate $Cr(CO)_4$ complex, providing evidence for the ability of this anion to behave as a Lewis acid through its electron-deficient system. Communications describing preliminary results have appeared [7].

Results and discussion

Reactions with 1,10-phenanthroline

Reactions of $K[Cr_2H(CO)_{10}]$ (I) with phen at salt/ligand molar ratios from 1/1 to 1/6, both in aqueous or anhydrous alcohols between room temperature and 50°C for various times take place almost exclusively according to eq. 1.

$$\underset{(I)}{K[Cr_2H(CO)_{10}]} + 3\ \text{phen} \rightarrow \underset{(II)}{K[Cr_2H(CO)_{10}(\text{phen})_3]} \qquad (1)$$

Reaction 1 at room temperature gave II in virtually quantitative yield, and with water/ethanol solutions the product readily separated as a crystalline yellow solid. The use of an excess or deficiency of the ligand resulted either in free phen (recovered from the colourless solution), corresponding in amount to the used excess, or unreacted I, and corresponding lower yields of II, respectively; in this latter case further addition of phen to the residual solution of I, in such amount that the required 3/1 molar ratio was produced, gave more II, up to its usual overall yield. No clear evidence for formation of adducts having other stoichiometries was found. Trace amounts of the known deep-red phen$Cr(CO)_4$ complex were observed to form at room temperature. Variable small amounts were produced with long reaction times or higher temperatures; even after three days with warming at 45—50°C for 5 h, only about 14% of it was obtained. It formed readily in larger amounts above 65°C. Solid II decomposed to give this complex when it was heated above 106°C; after 2 h at 120—126°C, it gave ca. 50% of phen$Cr(CO)_4$.

II was a rather stable compound. It was found to undergo partial dissociation, as indicated in eq. 2, in dilute CH_2Cl_2 solution, from which compound III separated on addition of petroleum ether.

$$K[Cr_2H(CO)_{10}(\text{phen})_3] \rightarrow \underset{(III)}{K[Cr_2H(CO)_{10}(\text{phen})_2]} \qquad (2)$$

This adduct was isolated in satisfactory yield from reactions at a 1/2 I/phen ratio (See Experimental). However, variation in the experimental conditions (excess of ligand, concentration, etc.) gave more II.

Since potassium salts react with 1,10-phenanthroline in non-aqueous solvents to give complexes containing up to a maximum of two moles of ligand [8—10], III might be expected as a main and more stable product under conditions which give II. The formation of II instead of III would indicate either (a) a preference of this alkali metal ion to react with this ligand to give a tris-phen-potassium complex species when it is associated with certian anions such as the title complex anion, or (b) a coordinative interaction between one mol of phen and the Cr—H—Cr system in addition to formation of a bis-phen-potassium complex species. However there was no clear evidence for such reaction in II. On the other hand, the interaction of phen with a potassium salt such as the tetraphenylborate gave exclusively a 3/1 adduct [11]. The IR spectra of tetrahydrofuran (THF) or CH_2Cl_2 solutions of the two compounds in the ν(CO) region (Fig. 1) are similar to one another and to that of THF solutions of I (i.e., they exhibit the three ν(CO) frequencies expected for the linear three-center system of the complex anion free from any interaction) whereas those obtained with nujol mulls indicate a rather distorted configuration in the solid compounds, probably induced by the complex cations present. This influence is more clearly indicated in the IR spectrum of III than in that of II. But the presence of the potassium counter-ion, with its tendency to form complex species with the ligand, was a serious handicap to detect a coordinative participation of the complex anion in II from the spectroscopic data. Results of infrared and Raman investigations on these compounds will be discussed elsewhere [12].

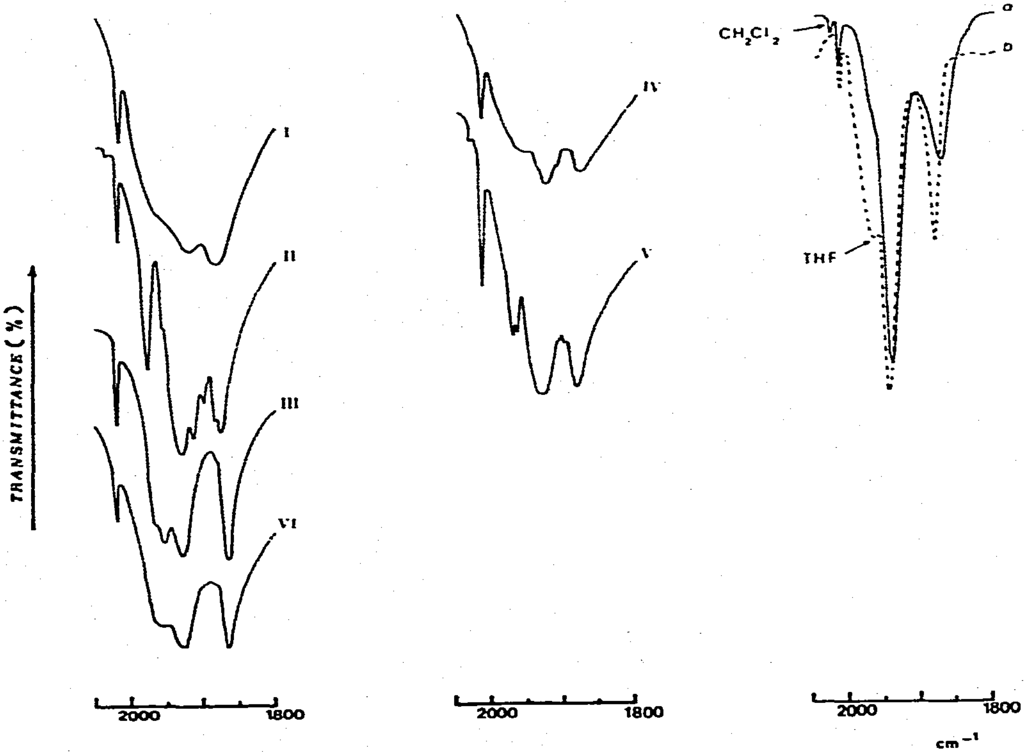

Fig. 1. IR spectra of starting salts and complexes in the carbonyl stretching frequency region in nujol, THF and CH_2Cl_2. Positions of bands with CH_2Cl_2 solutions (a): 2038m, 1942vs, 1878s cm^{-1}. Positions of bands with THF solutions (b): 2038m, 1946vs, 1884s cm^{-1}.

Such a participation of the anion was demonstrated, however, for the reactions involving $(C_4H_9)_4NCr_2H(CO)_{10}$ (IV). After reactions with phen in solvents such as acetone or CH_2Cl_2 at 1/1 molar ratios, evaporation afforded the adduct $(C_4H_9)_4N[Cr_2H(CO)_{10}(phen)]$ (V). This compound, which readily dissociates in solution and is unstable in air and moisture, was satisfactorily recrystallized. The IR spectra on nujol mulls of recrystallized or crude samples of V when compared with that of a solid mixture of the reactants, showed that a definite compound had been produced. There is no indication of the presence of free phen, and the number of ν(CO) frequencies observed (Fig. 1) show a hindered structure for $Cr_2H(CO)_{10}^-$; this cannot in this case be attributed to the influence of complex cation, but may be the result of a base—acid interaction of the ligand with its electron-deficient Cr—H—Cr system.

Reactions with 2,2'-bipyridine

Various sets of conditions were used for the reaction of I with bpy. The product $K[Cr_2H(CO)_{10}(bpy)_2]$ (VI) was obtained under conditions similar to those used for II. No adduct other than VI was detected. VI was obtained from reactions at 1/3 I/bpy molar ratios in water/ethanol; it separated on partial evaporation of the reaction solution (excess bpy remained in the solution) and was pure enough to give satisfactory characterization data. Unlike III, VI was unstable; thus the ligand was easily removed by use of solvents (toluene, e.g.) in which it is the only soluble component, and I released by addition of solvents such as n-heptane or petroleum ether. When VI was treated with CH_2Cl_2, I was readily released in 40—60% yield depending on the concentration; the remainder was kept in solution by the presence of the ligand in excess. Addition of petroleum ether to the residual solution caused crystallization of VI; however the yield was variable and sometimes very low, since a minor variation of conditions could cause separation of further I. This latter dissolved in CH_2Cl_2 rather readily, as a consequence of complex formation, when 1/4—1/5 I/bpy ratios were used; the dissolution was also influenced by the solution concentration. Crystals of pure VI separated on cooling such solutions at —60°C. Comparison of the IR spectra (nujol mulls) with that of a separately prepared mixture show VI to be a definite compound. There is no indication of free bpy, and the ν(CO) region (Fig. 1) resembles that of the mull spectrum of III, which suggest the presence in VI of an analogous but unknown bis-bpy potassium complex which induces a similar distortion of the complex anion. However, on attempting to isolate a bis-bpy complex with potassium tetraphenylborate, we could not obtain any adduct other than the 1/1 species [11]. To data no complexes of potassium salts with bpy have been found.

Reactions of IV with bpy under various conditions gave no evidence of adduct formation. Evaporation of acetone or CH_2Cl_2 solutions containing a 1/1 IV/bpy ratio afforded a yellow sticky residue, the mull spectrum of which was similar to that of a separately prepared mixture.

Experimental

All operations were carried out under nitrogen with carefully deaerated solvents. $Cr(CO)_6$ was prepared by the method of Ercoli et al. [13]. 1,10-Phenan-

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TABLE 1

SOME PROPERTIES AND ANALYSES OF $Cr_2H(CO)_{10}^-$ SALTS AND COMPLEXES

Compound	Colour	M.p. (dec.) (°C)	τ(M—H) (ppm)	Analysis (found (calcd.) (%))				
				C	H	N	Cr	K
I	gold-yellow	200 [a]	29.10	28.13 (28.31)	0.30 (0.24)		24.53 (24.51)	9.06 (9.21)
II	orange-yellow	112—115 [b]	28.70	57.19 (57.26)	2.59 (2.61)	8.70 (8.71)	10.60 (10.78)	4.02 (4.05)
III	yellow	106—109 [b]	28.90	51.92 (52.04)	2.10 (2.18)	7.18 (7.14)	12.90 (13.26)	4.89 (4.98)
IV	light-yellow	70—71	29.45	49.92 (49.75)	5.87 (5.94)	2.26 (2.23)	16.42 (16.57)	
V	pale-yellow	76—77	28.89	56.52 (56.50)	5.68 (5.61)	5.22 (5.20)	12.82 (12.87)	
VI	yellow	118—119	28.90	48.56 (48.92)	2.29 (2.33)	7.72 (7.61)	13.86 (14.12)	5.28 (5.31)

[a] The compound greened giving $Cr(CO)_6$. [b] The complexes became red without melting at this temperature.

throline, 2,2'-bipyridine, $(C_4H_9)_4NBr$ and solvents were reagent grade and were used as received, unless otherwise stated. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn. Melting points (decomp.) were determined in capillaries sealed under vacuum and are uncorrected. IR spectra were recorded with nujol mulls and THF or CH_2Cl_2 solutions on a Perkin—Elmer mod. 577 instrument, and ^1H NMR spectra in $(CD_3)CO$ solutions on a Jeol 60 HL spectrometer. Some properties and analytical and ^1H NMR data of the compounds prepared are listed in Table 1.

Preparation of K[$Cr_2H(CO)_{10}$] (I)

$Cr(CO)_6$ (36 g, 0.16 mol) was added to a solution of potassium hydroxide (63 g, 1.12 mol) in a minimum of water (75 mol) *, methanol (300 ml) and tetrahydrofuran (THF) (720 ml). The suspension stirred at 45—50°C for 5 h, during which an orange-red solution and a white solid (potassium carbonate), were produced. The mixture was stirred for a further 14 h at room temperature, then filtered. [The solid was heated at 60°C in vacuo using an acetone-dry ice trap at —78°C to confirm absence of unreacted $Cr(CO)_6$.] The filtrate was almost completely evaporated under vacuum at 40—50°C to leave a yellow-orange paste (mixture of potassium derivatives of known chromium carbonyl anions) to which water (820 ml) was added. The mixture was stirred at room temperature for about 24 h, during which time hydrogen was slowly evolved and the yellow crystalline salt separated. After stirring for a further 23 h ** at 3—5°C, the mixture was filtered, the solid washed with cold water, and dried under high vacuum (29.1 g, yield 83.8%). Usual yields were 73—84%. I is very soluble in ethanol, acetone and THF, almost insoluble in CH_2Cl_2, and somewhat soluble in water, from which it was crystallized in 60—70% yield. Care to avoid warming above

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* The use of more water was observed to lead also to a green phase which had to be removed before filtration.

** The use of longer times causes formation of some $Cr(CO)_6$.

50°C, and rapid bandling prevented the separation of $Cr(CO)_6$). Although very air-sensitive in solution, the well dried compound decomposes only slowly. (Usually the greenish oxidation product can be filtered off from its solutions.) It also seems to be light-sensitive.

Preparation of $K[Cr_2H(CO)_{10}(phen)_3]$ *(II)*

A filtered ethanolic solution of I (1.9 g, 4.48 mmol in 30 ml) was slowly added to a stirred water/ethanol solution (2/1, v/v) of monohydrate phen (3.0 g, 15 mmol in 90 ml). Yellow crystals soon formed. The mixture was stirred at room temperature for 1 h, then partly evaporated (ca. 50 ml) in vacuo at 40—45°C. The solid was collected by filtration, washed with water/ethanol (3/1, v/v), and dried under high vacuum (4.15 g, yield 96.06/). The product was dissolved in 95% ethanol (50 ml) by a brief warming to 45°C, and after filtration toluene was added (15 ml), to throw out phen$Cr(CO)_4$ impurities. Vacuum removal of ca. 20 ml of solvent at 40°C and cooling at —50°C for 5 h gave orange-crystals which were filtered off, washed with toluene, and dried in vacuo. The filtrate and washing, were further concentrated (ca. 15 ml) and cooled to give more II, (3.9 g, yield 93.9%). The product is very soluble in acetone and THF, soluble in methanol weakly soluble in CH_2Cl_2, and slightly soluble in toluene. Solid II is air-stable and can be stored in the dark for a long time, but its solutions soon become red because of formation of phen$Cr(CO)_4$.

Preparation of $K[Cr_2H(CO)_{10}(phen)_2]$ *(III)*

Phen/H_2O (1.11 g, 5.6 mmol) was added to a filtered acetone solution of I (1.2 g, 2.8 mmol in 50 ml), and the solution was stirred at room temperature for 1 h, then evaporated to dryness in vacuo at 40°C. The yellow residue was treated with dry CH_2Cl_2 (120 ml) at room temperature and the residual solid (a mixture of II and I) filtered off. Petroleum ether (30—50°C) was slowly added (45 ml) with stirring until shining yellow crystals appeared. After ca. 1 h these were filtered, washed with petroleum ether and dried in vacuo. The filtrate and washing gave more crystals on addition of more solvent. The identity of the samples was checked by mull spectra (yield 1.4 g, 63.5%). The compound is soluble in the common polar solvents, and slightly soluble in water. It is air-stable in the solid state, but appeared to decompose more easily than II in solution to give phen$Cr(CO)_4$.

Preparation of $(C_4H_9)_4NCr_2H(CO)_{10}$ *(IV)*

A solution of $(C_4H_9)_4NBr$ (1.52 g, 4.7 mmol) dissolved in 20 ml of dry distilled acetone was added to a filtered solution of I (1.8 g, 4.24 mmol) in the same solvent (40 ml). The mixture was stirred at room temperature for 1 h, the KBr precipitate filtered off, and the yellow filtrate evaporated to dryness in vacuo. The yellow viscous residue was dissolved in 95% ethanol (100 ml), and after filtration water, at 50—60°C was added with manual stirring until there was a turbidity which disappeared on short warming. The solution was left to stand at room temperature for ca. 1 h to give yellow needles, which were filtered off, washed with water, and dried under high vacuum. Filtrate and washing gave more crystals which were collected as before (2.43 g, yield 91.3%). The compound is soluble in the common polar solvents and insoluble in water. The solid

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