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Preparation of Acetylene-Alcohol Dicobalt Hexacarbonyls and Their Reactivity towards Acid

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A series of acetylene-alcohol dicobalt hexacarbonyls was prepared from acetylene-alcohols and dicobalt octacarbonyl. The reactivity towards aqueous sulfuric acid in boiling methanol was investigated. From the ethynyl carbinol complexes, $R^1R^2C(OH)C{\equiv}CH\cdot Co_2(CO)_6$, trinuclear cobalt complexes, $R^1R^2CHCH_2CCo_3(CO)_9$, were obtained accompanying the reduction of C–OH to a C–H moiety. On the other hand, from the butynediol complexes, $R^1R^2C(OH)C{\equiv}CC(OH)R^1R^2\cdot Co_2(CO)_6$, binuclear cobalt complexes, $R^1R^2CHC{\equiv}CCHR^1R^2\cdot Co_2(CO)_6$, or 1,1,4,4-tetraphenyl-1,3-butadiene were obtained. The structures of all these compounds have been confirmed by analytical measurements and by a study of their absorption spectra.

It is well known that acetylenes readily displace the two bridge carbonyl groups in dicobalt octacarbonyl to yield acetylenic dicobalt hexacarbonyls.[1,2] As a part of the study of the chemical behavior of these complexes, the reaction of acetylenic dicobalt hexacarbonyls, $RC{\equiv}CH\cdot Co_2(CO)_6$, (derived from terminal acetylenes) with aqueous mineral acids in boiling alcohol to yield trinuclear cobalt complexes, $RCH_2CCo_3(CO)_9$, has been reported on.[3]

In this paper, the preparation of various acetylene-alcohol dicobalt hexacarbonyls derived from the ethynyl carbinols and the butynediols, and the treatment of these complexes with aqueous sulfuric acid in boiling methanol will be reported.

Results and Discussion

Preparation of Acetylene-alcohol Dicobalt Hexacarbonyls. Various ethynyl carbinols and butynediols have now been treated with dicobalt octacarbonyl in diethyl ether or petroleum ether at room temperature under nitrogen for 2 hr to give red to reddish-brown acetylene-alcohol dicobalt hexacarbonyls. The properties of and analytical data on these complexes are summarized in Table 1. The spectra of each of the acetylene-alcohol dicobalt hexacarbonyls contain characteristic groups of three or four sharp bands in the range from 2000 to 2200 cm^{-1}; these bands are attributable to the terminal carbonyl groups. The band characteristic of the bridge carbonyl groups near 1800 cm^{-1} is absent. The band of the acetylenic C–H stretching at 3300 cm^{-1} in the starting materials was shifted by the complex formation to 3100 cm^{-1}, a characteristic olefinic C–H stretching frequency. The band characteristic of the carbon-carbon triple bond is absent. The PMR spectrum of ethynyl carbinol complexes shows a sharp singlet signal near τ 4.0 assignable to the coordinated terminal acetylenic proton.

Reactivity towards Aqueous Sulfuric Acid in Boiling Methanol. Ethynyl carbinol dicobalt hexacarbonyls have been treated with aqueous sulfuric acid in boiling methanol for 2 hr. Sublimable crystals, from dark purple to dark brown, were obtained. They were easily soluble in petroleum ether and were crystallized from methanol by deep cooling. The trinuclear structure for these compounds is supported by the results of the elemental analyses

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[1] H. W. Sternberg, H. Greenfield, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

[2] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *ibid.*, **78**, 120 (1956).

[3] R. Markby, I. Wender, R. A. Friedel, F. A. Cotton and H. W. Sternberg, *ibid.*, **80**, 6529 (1958).

TABLE 1. ACETYLENE-ALCOHOL DICOBALT HEXACARBONYLS

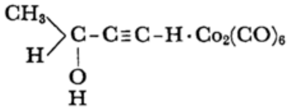
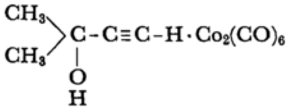
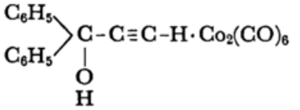
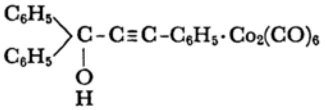
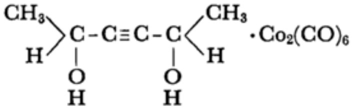
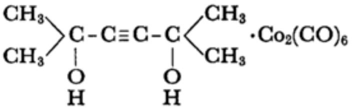
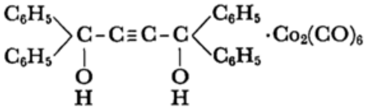
Compound	Description	Mp °C	Analyses, % Calcd C	Analyses, % Calcd H	Analyses, % Found C	Analyses, % Found H
 $\mathrm{(CH_3)(H)C(OH)-C{\equiv}C-H\cdot Co_2(CO)_6}$	Red crystals	36—38	33.74	1.70	33.56	1.64
 $\mathrm{(CH_3)_2C(OH)-C{\equiv}C-H\cdot Co_2(CO)_6}$	Red crystals	42—43.5	35.70	2.18	35.86	2.30
 $\mathrm{(C_6H_5)_2C(OH)-C{\equiv}C-H\cdot Co_2(CO)_6}$	Red crystals	125 (dec.)	51.04	2.45	51.02	2.69
 $\mathrm{(C_6H_5)_2C(OH)-C{\equiv}C-C_6H_5\cdot Co_2(CO)_6}$	Reddish brown crystals	95 (dec.)	56.86	2.83	56.92	3.04
 $\mathrm{(CH_3)(H)C(OH)-C{\equiv}C-C(OH)(CH_3)(H)\cdot Co_2(CO)_6}$	Red crystals	100 (dec.)	36.02	2.52	36.06	2.67
 $\mathrm{(CH_3)_2C(OH)-C{\equiv}C-C(OH)(CH_3)_2\cdot Co_2(CO)_6}$	Reddish brown crystals	110 (dec.)	39.27	3.30	39.18	3.32
 $\mathrm{(C_6H_5)_2C(OH)-C{\equiv}C-C(OH)(C_6H_5)_2\cdot Co_2(CO)_6}$	Reddish brown crystals	115 (dec.)	60.37	3.28	60.24	3.33

TABLE 2. INFRARED SPECTRA OF $R^1R^2CHCH_2CCo_3(CO)_9$ IN KBr DISK (cm^{-1})

$CH_3CH_2CCo_3(CO)_9$	642	554,	532,	520	506	474
$CH_3CH_2CH_2CCo_3(CO)_9$	659	557,	543,	532	506	475
$(CH_3)_2CHCH_2CCo_3(CO)_9$	660	556,	542,	532	506	475
$(C_6H_5)_2CHCH_2CCo_3(CO)_9$	582	532,	526,	518	504	455
Suggested assignment*	RC-Co stretch			Co-CO stretch		

* Ref. 4

and of the molecular-weight determinations (cryoscopy in benzene), and by their absorption spectra. The infrared spectra of these compounds show the absence of a hydroxyl group and the presence of terminal carbonyl groups. The stretching frequency of the C–Co bond was observed to be as shown in Table 2. The band near 650 cm^{-1} is susceptible to the alkyl groups, while those in the 470—560 cm^{-1} region are almost independent of the alkyl groups.[4] The PMR spectra of these trinuclear cobalt complexes are summarized in Table 3. The spectra are in good agreement with the $R^1R^2CHCH_2CCo_3(CO)_9$ structure. The chemical shift of the methylene proton neighboring the $CCo_3(CO)_9$ group is observed in the lower field, *e.g.*, near τ 6.3. This may be caused by the strong electron affinity of the $Co_3(CO)_9$ group.

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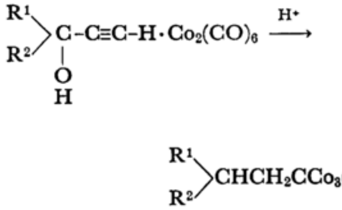
4) W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed and B. L. Shaw, *Proc. Chem. Soc.*, **1961**, 169.

TABLE 3. PROTON MAGNETIC RESONANCE DATA OF $R^1R^2CHCH_2CCo_3(CO)_9$ COMPLEXES AT 60 Mc/sec

Compound	Band position, τ	Relative intensity	Assignment	Coupling constant
$CH_3CH_2CCo_3(CO)_9$	8.46 (triplet)	3	CH_3	$J=7.5$ cps
	6.22 (quartet)	2	CH_2	$J=7.5$ cps
$CH_3CH_2CH_2CCo_3(CO)_9$	8.84 (triplet)	3	CH_3	$J=7.0$ cps
	8.09 (multiplet)	2	CH_2	
	6.35 (triplet)	2	CH_2	$J=7.0$ cps
$(CH_3)_2CHCH_2CCo_3(CO)_9$	8.81 (doublet)	6	CH_3	$J=5.5$ cps
	7.8—8.3 (multiplet)	1	CH	
	6.33 (doublet)	2	CH_2	$J=5.5$ cps



$$\underset{R^2}{\overset{R^1}{>}}C(OH)-C\equiv C-H\cdot Co_2(CO)_6 \xrightarrow{H^+} \underset{R^2}{\overset{R^1}{>}}CHCH_2CCo_3(CO)_9$$

The $(CH_3)_2CHCH_2CCo_3(CO)_9$ complex was also formed from the ether complex $(CH_3)_2C(OCH_3)C\equiv CH\cdot Co_2(CO)_6$ under conditions analogous to those described above. The $CH_3CH_2CH_2CCo_3(CO)_9$ complex has also been obtained from vinylacetylene dicobalt hexacarbonyl $CH_2=CH-C\equiv CH\cdot Co_2(CO)_6$ by treatment with aqueous sulfuric acid in boiling methanol.[5)]

Secondly, butynediol dicobalt hexacarbonyls have been treated with aqueous sulfuric acid in boiling methanol for 30 min. From tetramethylbutynediol dicobalt hexacarbonyl, brown crystals were obtained. The infrared spectra of this compound showed the absence of a hydroxyl group and the presence of terminal carbonyl groups. The PMR spectra in hexadeuterobenzene showed a doublet centered at τ 8.91[*1] and a multiplet in the range from τ 6.9 to 7.6 with a relative intensity of 6 : 1. The analytical data of the elements were consistent with the composition in which two oxygen atoms were eliminated from the starting compound. Therefore, this compound seems to be di-isopropylacetylene dicobalt hexacarbonyl.[*2] On the other hand, from tetraphenylbutynediol dicobalt hexacarbonyl, 1,1,4,4-tetraphenyl-1,3-butadiene was obtained.

In the well-known Meyer-Schuster Rearrangement free acetylenic carbinols are rearranged into unsaturated ketones or aldehydes by acidic reagents. In the present study, acetylenic carbinols coordinated to cobalt atoms were found not to take the Meyer-Schuster Rearrangement, but to be reduced and to form trinuclear cobalt complexes. As cobalt sulfate was recognized in an aqueous solution, the reduction of acetylene-alcohol may occur through the oxidation of Co^0 to Co^{2+} by the partial decomposition of the starting cobalt(0) complex. The hydrido cobalt carbonyl intermediate has been postulated for the formation of the trinuclear cobalt complex.[6)] However, the reaction of $(CH_3)_2C(OH)C\equiv CH\cdot Co_2(CO)_6$ with $HCo(CO)_4$ in methanol was found to yield $(CH_3)_2CHC\equiv CH\cdot Co_2(CO)_6$[*3] as the reduction product. The trinuclear cobalt complex $(CH_3)_2CHCH_2CCo_3(CO)_9$ was not formed. It remains to be proved how the reduction of C–OH to the C–H moiety occurs in the progress of the formation of the trinuclear cobalt complex.

Experimental

All melting points are uncorrected; they were measured by a micro melting point apparatus, Yanagimoto Model MP-S2. The infrared spectra were obtained by a Jasco Model DS-402 G grating spectrometer. The PMR spectra were recorded by a Varian Model A-60 instrument in carbon tetrachloride using tetramethylsilane as an internal standard. The molecular weights were measured by the cryoscopic method in benzene, using the vaporphase osmometer instrument developed by Dr.-Ing. Herbert Knauer.

Materials. The propargyl alcohol and 1-butyne-3-ol (35% in water) were of a Tokyo Kasei Reagent Grade. The 3-methyl-1-butyne-3-ol, 3-hexyne-2,5-diol, and 2,5-dimethyl-3-hexyne-2,5-diol were obtained from our laboratory. The ethynylbenzhydrol,[7)] 3-phenylethynylbenzhydrol,[8)] 1,1,4,4-tetraphenyl-2-butyne-1,4-diol,[9)] and dicobalt octacarbonyl[10)] were prepared by the methods described in the literature.

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5) I. Kaneko and N. Hagihara, unpublished result.

6) G. Albanesi and E. Gavezzotti, *Chim e l'ind* (*Milan*), **47,** 1322 (1965).

[*1] The coupling constant was 7.0 cps.

[*2] Added in Proof: From $(C_6H_5)_2C(OH)C\equiv CC_6H_5\cdot Co_2(CO)_6$, $(C_6H_5)_2CHC\equiv CC_6H_5\cdot Co_2(CO)_6$ was obtained by a method analogous to that described above. Reddish-brown crystals, mp 88—91°C. PMR: τ 2.60—3.00 (m) and 4.50 (s), with a relative intensity of 15 : 1 in CCl_4 at 60 Mc/sec.

[*3] Satisfactory elemental analyses have been obtained. PMR spectra: τ 4.13 (s), 6.85—7.30 (m) and 8.72 (d) ($J=7.0$ cps), with a relative intensity of 1 : 1 : 6 in CCl_4 at 60 Mc/sec.

7) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, **1963,** 2707.

8) K. Hess and W. Weltzien, *Ber.*, **54,** 2511 (1921).

9) A. Zweig and A. K. Hoffmann, *J. Am. Chem. Soc.*, **84,** 3278 (1962).

10) R. B. King, *Organometal. Syn.*, **1,** 99 (1965).

The Preparation of Acetylene-alcohol Dicobalt Hexacarbonyls. The ethynyl carbinols or butynediols and dicobalt octacarbonyl were allowed to react at room temperature for 2 hr in diethyl ether under a nitrogen atmosphere. Stoichiometric amounts or an excess of the acetylene-alcohols were used, depending upon the subsequent purification procedure. The reaction mixture was usually filtered to remove any insoluble impurities, and the filtrate was evaporated *in vacuo*. The residue was then purified by recrystallization from methanol on deep cooling or by molecular distillation.

A description of the compounds and the analytical data are given in Table 1. The preparation of $(CH_3)_2C(OH)$-$C\equiv CH\cdot Co_2(CO)_6$ will be described in detail below: To a solution of 4.3 g (51 mmol) of $(CH_3)_2C(OH)C\equiv CH$ in 100 m*l* of diethyl ether, there were added 14 g (41 mmol) of dicobalt octacarbonyl under nitrogen. The mixture was stirred for 2 hr and then filtered. The filtrate was concentrated by a water aspirater and crystallized from methanol at $-78°C$. Red crystals, mp 42—43.5°C, were obtained (yield, 15 g, 98%).

The Preparation of 3-Methyl-3-methoxyl-1-butyne Dicobalt Hexacarbonyl, $(CH_3)_2C(OCH_3)C\equiv CH\bullet CO_2(CO)_6$. To a solution of 1.5 g (14.6 mmol) of 3-methyl-3-chloro-1-butyne[11] in 60 m*l* of diethyl ether, there were added 7.5 g (21.9 mmol) of dicobalt octacarbonyl under a nitrogen atmosphere. The mixture was stirred for 2 hr. Twenty milliliters of methanol were then added, after which the mixture was stirred for 45 min, washed with water, and extracted with diethyl ether. After drying over sodium sulfate and concentration, the residue was submitted to molecular distillation at 60—70°C/1 mmHg with a cold finger cooled by dry ice-acetone. 2.83 g of a deep red oil were obtained (yield, 50.5%). PMR: τ 8.50 (s) (CH_3), 6.77 (s) (OCH_3) and 3.99 (s) (CH) with a relative intensity of 6 : 3 : 1.

Found: C, 38.14; H, 2.61%. Calcd for $C_{12}H_{10}O_7$-Co_2: C, 37.53; H, 2.62%.

The Formation of Trinuclear Cobalt Complexes $R^1R^2CHCH_2CCo_3(CO)_9$. **$CH_3CH_2CCo_3(CO)_9$.** Propargyl alcohol dicobalt hexacarbonyl (prepared from 2 g of propargyl alcohol and 5 g of dicobalt octacarbonyl) was dissolved in 60 m*l* of methanol. To this solution 10 m*l* of 10 N sulfuric acid were added, and the mixture was refluxed for 2 hr. After it had then been cooled to room temperature, the reaction mixture was diluted with 120 m*l* of water and extracted with petroleum ether. The organic layer was concentrated, and the residue was crystallized from methanol by cooling at $-78°C$. Violet crystals were obtained (yield, 560 mg).

Found: C, 30.46; H, 1.19%; mol wt, 477. Calcd for $C_{12}H_5O_9Co_3$: C, 30.67; H, 1.07%; mol wt, 470.

$CH_3CH_2CH_2CCo_3(CO)_9$. From $CH_3CH(OH)C\equiv CH\cdot Co_2(CO)_6$, dark violet crystals were obtained by a method analogous to that described above. Mp 110°C (dec.).

Found: C, 32.79; H, 1.49%. Calcd for $C_{13}H_7O_9$-Co_3: C, 32.27; H, 1.48%.

$(CH_3)_2CHCH_2CCo_3(CO)_9$. *a*) *From the Alcohol Complex:* A mixture of $(CH_3)_2C(OH)C\equiv CH\cdot Co_2(CO)_6$ (2 g), methanol (40 m*l*), and 10 N sulfuric acid (8 m*l*) was refluxed for 2 hr. After it had then been worked up, reddish violet crystals were obtained. Mp 105°C (yield, 270 mg).

Found: C, 34.12; H, 1.96%; mol wt, 517. Calcd for $C_{14}H_9O_9Co_3$: C, 33.76; H, 1.82%; mol wt, 498.

b) *From the Ether Complex:* A mixture of $(CH_3)_2C$-$(OCH_3)C\equiv CH\cdot Co_2(CO)_6$ (1.1 g), methanol (20 m*l*), and 10 N sulfuric acid (4 m*l*) was refluxed for 2 hr. After it had then been worked up, reddish violet crystals were obtained. The infrared spectra of this compound were consistent with those of that obtained in *a*).

$(C_6H_5)_2CHCH_2CCo_3(CO)_9$. From a mixture of $(C_6$-$H_5)_2C(OH)C\equiv CH\cdot Co_2(CO)_6$ (2 g), methanol (40 m*l*), and 10 N sulfuric acid (8 m*l*), brown crystals were obtained after a 2-hr reaction. Mp 124°C (dec.). (Yield, 310 mg).

Found: C, 46.17; H, 2.00%; mol wt, 643. Calcd for $C_{24}H_{13}O_9Co_3$: C, 46.33; H, 2.11%; mol wt, 622.

Di-isopropylacetylene Dicobalt Hexacarbonyl. A mixture of $(CH_3)_2C(OH)C\equiv CC(OH)(CH_3)_2\cdot Co_2$-$(CO)_6$ (2 g), methanol (20 m*l*), and 10 N sulfuric acid (8 m*l*) was refluxed for 30 min. After it had been cooled to room temperature, the reaction mixture was filtered and the precipitates were washed with water and dissolved in methanol. The filtrate was cooled by dry ice to give brown crystals, mp 95°C. (Yield, 370 mg).

Found: C, 42.19; H, 3.48%. Calcd for $C_{14}H_{14}O_6$-Co_2: C, 42.45; H, 3.56%.

1,1,4,4-Tetraphenyl-1,3-butadiene. To a solution of 1 g of $(C_6H_5)_2C(OH)C\equiv CC(OH)(C_6H_5)_2\cdot Co_2(CO)_6$ in 20 m*l* of methanol, 4 m*l* of 10 N sulfuric acid were added. The reaction mixture was then refluxed for 30 min. Yellow crystals were thus precipitated. These were filtered, washed with water, and dried. Recrystallization from benzene gave pale yellow prisms with a pale green fluorescence, mp 192(sinter)—204°C. (Yield, 162 mg). Recrystallization from ethanol gave pale yellow needles with a pale green fluorescence, mp 197—198°C.

Found: C, 93.72; H, 5.99%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%.

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[11] G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.* **79**, 2142 (1957).