Phosphite Complexes of Alkyl- and Acyl-Cobalt Carbonyls
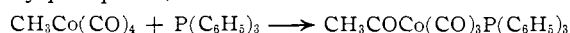
BY RICHARD F. HECK

Methylcobalt tricarbonyl triphenylphosphine reacts with trimethyl phosphite to form acetylcobalt dicarbonyl trimethyl phosphite triphenylphosphine. A similar compound was obtained from methoxymethylcobalt tricarbonyl triphenylphosphine. Heating methyl- or acetyl-cobalt tetracarbonyl with trimethyl phosphite leads to the formation of acetylcobalt dicarbonyl bis-(trimethyl phosphite). This complex is cleaved by sodium methoxide to methyl acetate and sodium cobalt dicarbonyl bis-(trimethyl phosphite). The latter compound reacts with methyl iodide to form methylcobalt dicarbonyl bis-(trimethyl phosphite) and this compound reacts with more trimethyl phosphite to give acetylcobalt carbonyl tris-(trimethyl phosphite). A similar series of compounds was prepared using trimethylolpropane phosphite in place of trimethyl phosphite. The acetylcobalt carbonyl tris-(trimethylolpropane phosphite) was cleaved with sodium ethoxide to ethyl acetate and sodium cobalt carbonyl tris-(trimethylolpropane phosphite). The latter compound reacted with methyl iodide to produce methylcobalt carbonyl tris-(trimethylolpropane phosphite). This compound did not react further with trimethylolpropane phosphite. The alkyl- and acyl-cobalt complexes become more stable as the number of phosphite ligands present increases.

Introduction

It is now well known that phosphine and phosphite ligands stabilize transition metal alkyls. Chatt[1] and Coates,[2] for example, have been able to prepare alkyl derivatives of group VIII metals by alkylation of the bisphosphine halide derivatives of these metals. Previously, we found it possible to prepare relatively stable acylcobalt tricarbonyl triphenylphosphine complexes by the reaction of alkyl- or acyl-cobalt tetracarbonyls with triphenylphosphine.[3] More recently Hieber has prepared the moderately stable methyl-[4] and phenyl-[5] cobalt tricarbonyl triphenylphosphines. Previous attempts to prepare poly-(triphenylphosphine) complexes of acylcobalt carbonyls were unsuccessful,[3] but it has now been found that certain phosphites will yield bis and tris as well as mono derivatives.

Results and Discussion

Since methylcobalt tetracarbonyl reacts with triphenylphosphine to give acetylcobalt tricarbonyl triphenylphosphine,[3] it was of interest to find out if

$$CH_3Co(CO)_4 + P(C_6H_5)_3 \longrightarrow CH_3COCo(CO)_3P(C_6H_5)_3$$

methylcobalt tricarbonyl triphenylphosphine[4] would react with another molecule of a phosphine and give a bisphosphine complex. The compound does not react with triphenylphosphine, as expected from our earlier findings that more than one triphenylphosphine group could not be added to these compounds,[3] but it did react with trimethyl phosphite. With only a small excess of the phosphite, acetylcobalt dicarbonyl trimethyl phosphite triphenylphosphine was formed as a yellow crystalline compound, m.p. 105–106.5° dec.

$$CH_3Co(CO)_3P(C_6H_5)_3 + P(OCH_3)_3 \longrightarrow$$
$$CH_3COCo(CO)_2[P(C_6H_5)_3]P(OCH_3)_3$$
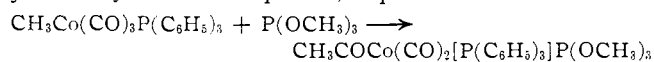
A similar compound was prepared from methoxyacetylcobalt tricarbonyl triphenylphosphine and trimethyl phosphite.

An attempt was made to prepare methylcobalt tricarbonyl trimethyl phosphite by the same method used to prepare the corresponding triphenylphosphine complex.[4] Trimethyl phosphite was allowed to react with cobalt octacarbonyl in the hope of obtaining dicobalt hexacarbonyl bis-(trimethyl phosphite) which could then be treated with sodium amalgam to form the sodium salt and finally alkylated with methyl iodide. Only a dark, intractable tar was obtained from the cobalt carbonyl–trimethyl phosphite reaction, however. Similar reactions with tris-(p-anisyl)-phosphine and

(1) J. Chatt and B. L. Shaw, J. Chem. Soc., 705 (1959); 285 (1961).
(2) G. Calvin and G. E. Coates, ibid., 2008 (1960).
(3) R. F. Heck and D. S. Breslow, J. Am. Chem. Soc., 84, 2499 (1962).
(4) W. Hieber and E. Lindner, Z. Naturforsch., 16b, 137 (1961).
(5) W. Hieber and E. Lindner, Chem. Ber., 95, 273 (1962).

trimethylolpropane phosphite [1,1,1-tris-(hydroxymethyl)-propane phosphite][6] were successful, however, and other polyphosphorus derivatives can be prepared from these compounds.

Methylcobalt tricarbonyl triphenylphosphine reacts with excess trimethyl phosphite to give acetylcobalt dicarbonyl bis-(trimethyl phosphite) as a nearly colorless crystalline compound, m.p. 35°. The same product

$$CH_3Co(CO)_3P(C_6H_5)_3 + 2P(OCH_3)_3 \rightleftarrows$$
$$CH_3COCo(CO)_2[P(OCH_3)_3]_2 + P(C_6H_5)_3$$
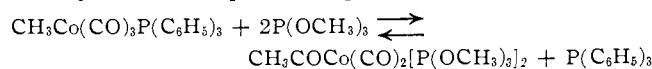
can also be obtained directly and more conveniently by heating acetyl- or methyl-cobalt tetracarbonyl with excess trimethyl phosphite in ether solution at about 75° for an hour in a closed container. Further heating,

$$CH_3COCo(CO)_4 + 2P(OCH_3)_3 \longrightarrow$$
$$CH_3COCo(CO)_2[P(OCH_3)_3]_2 + 2CO$$
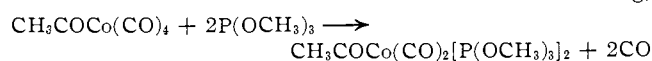
even with carbon monoxide removal, does not lead to any of the tris-(trimethyl phosphite) derivative.

As with the acylcobalt tetracarbonyls and tricarbonyl triphenylphosphines,[3] the acylcobalt dicarbonyl bis-phosphites can be cleaved by sodium methoxide to a methyl ester and a sodium carbonylate salt. Thus, acetylcobalt dicarbonyl bis-(trimethyl phosphite) gave methyl acetate and sodium cobalt dicarbonyl bis-(trimethyl phosphite). The sodium salt was obtained

$$CH_3COCo(CO)_2[P(OCH_3)_3]_2 + NaOCH_3 \longrightarrow$$
$$CH_3COOCH_3 + NaCo(CO)_2[P(OCH_3)_3]_2$$
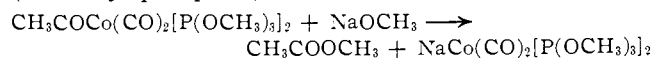
as colorless crystals, but it was pyrophoric and was not analyzed. It reacted very rapidly with methyl iodide in tetrahydrofuran solution, producing methylcobalt dicarbonyl bis-(trimethyl phosphite), a pale yellow crystalline compound, m.p. 50°. This compound had no acyl carbonyl absorption in the infrared region.

$$NaCo(CO)_2[P(OCH_3)_3]_2 + CH_3I \longrightarrow$$
$$CH_3Co(CO)_2[P(OCH_3)_3]_2 + NaI$$
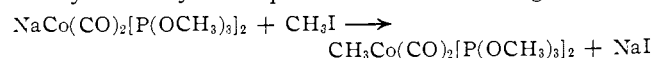
Methylcobalt dicarbonyl bis-(trimethyl phosphite) will react further with trimethyl phosphite to produce acetylcobalt carbonyl tris-(trimethyl phosphite) as yellow-green crystals, m.p. 49–50°. This material

$$CH_3Co(CO)_2[P(OCH_3)_3]_2 + P(OCH_3)_3 \longrightarrow$$
$$CH_3COCo(CO)[P(OCH_3)_3]_3$$
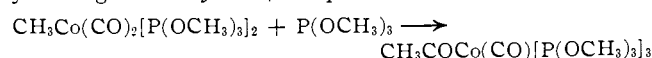
has a strong acyl carbonyl band in its infrared spectrum at 6.20 μ.

A similar series of reactions has been carried out with 1,1,1-trimethylolpropane phosphite,[6] TMPP, in place of trimethyl phosphite. The same reactions were observed but these derivatives were considerably easier to isolate because they were higher melting and less sol-

(6) W. S. Wadsworth, Jr., and W. D. Emmons, J. Am. Chem. Soc., 84, 610 (1962).

TABLE I

CARBONYL BANDS OF PHOSPHITE DERIVATIVES OF METHYL- AND ACETYL-COBALT TETRACARBONYLS

Compound	Solvent	Coördinated carbonyl bands, μ	Acyl carbonyl band, μ
$CH_3COCo(CO)_4{}^a$	$C_2H_5OC_2H_5$	4.77(m), 4.90(s), 4.95–5.00(vs)	5.82(s)
$CH_3COCo(CO)_3[P(OCH_3)_3]$	$C_2H_5OC_2H_5$	4.86(w), 5.01–5.09(vs)	5.93(s)
$CH_3COCo(CO)_2[P(OCH_3)_3]_2$	CCl_4	5.00(s), 5.16(vs)	6.03(s)
$CH_3Co(CO)_2[P(OCH_3)_3]_2$	CCl_4	5.01(s), 5.17(vs)	. . .
$CH_3COCo(CO)[P(OCH_3)_3]_3$	CCl_4	5.03(m), 5.10(m), 5.20(vs)	6.20(s)
$CH_3COCo(CO)_3(TMPP)$	CCl_4	4.82(m), 4.88–4.99(vs)	5.91(vs)
$CH_3Co(CO)_3(TMPP)$	THF	?4.85(vw), 4.92–5.12^b(vs)	. . .
$CH_3COCo(CO)_2(TMPP)_2$	CH_2Cl_2	4.93(s), 5.10(vs)	6.05(vs)
$CH_3Co(CO)_2(TMPP)_2$	CH_2Cl_2	4.99(s), 5.13(vs)	. . .
$CH_3COCo(CO)(TMPP)_3$	CH_2Cl_2	5.02(m), 5.12(vs)	6.16(s)
$CH_3Co(CO)(TMPP)_3$	CH_2Cl_2	5.04(vs), ?5.15(s)	. . .

^{a} Reference 7. ^{b} A weak ether or tetrahydrofuran band also occurs in this region.

uble. The complete group of compounds were prepared in this series: the methyl- and acetyl-cobalt tricarbonyl mono-(trimethylolpropane phosphite), methyl- and acetyl-cobalt dicarbonyl bis-(trimethylolpropane phosphite) and the methyl- and acetyl-cobalt monocarbonyl tris-(trimethylolpropane phosphite). This series was carried one step further than the trimethyl phosphite series. Acetylcobalt carbonyl tris-(trimethylolpropane phosphite) was cleaved with sodium ethoxide in tetrahydrofuran to ethyl acetate and sodium cobalt carbonyl tris-(trimethylolpropane phosphite).

$$CH_3COCo(CO)(TMPP)_3 + NaOC_2H_5 \longrightarrow$$
$$C_2H_5OCOCH_3 + NaCo(CO)(TMPP)_3$$
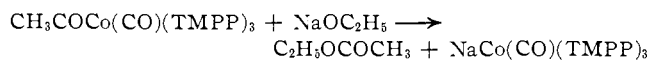
Alkylation of the sodium salt with methyl iodide gave methylcobalt carbonyl tris-(trimethylolpropane phosphite) as a colorless crystalline compound which decomposed at about 185°.

$$NaCo(CO)(TMPP)_3 + CH_3I \longrightarrow CH_3Co(CO)(TMPP)_3 + NaI$$
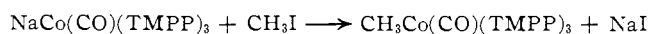
The compound has only a single carbonyl band, at 5.06 μ, in the infrared region. It does not react further with trimethylolpropane phosphite. Presumably no reaction takes place because there is not enough room around the cobalt atom for another large ligand.

The stability of the alkyl- and acyl-cobalt complexes increases with substitution of carbonyl groups by phosphite groups. The bis and tris derivatives are stable indefinitely at room temperature under nitrogen but they do undergo oxidation in the air slowly.

It is now possible to prepare a large variety of other phosphite derivatives of organocobalt complexes from these alkyl and acyl complexes. For example, acetylcobalt dicarbonyl bis-(trimethylolpropane phosphite) was hydrogenated with 3000 p.s.i. of hydrogen at 60° to produce cobalt dicarbonyl bis-(trimethylolpropane phosphite) hydride.

$$CH_3COCo(CO)_2(TMPP)_2 + H_2 \longrightarrow$$
$$CH_3CHO + HCo(CO)_2(TMPP)_2$$
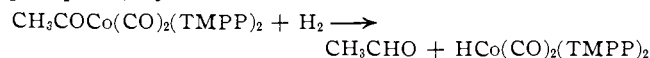
The hydride is a tan crystalline complex, m.p. 155–160° dec. It is stable at room temperature under nitrogen but is oxidized fairly rapidly by air.

The infrared spectra of the new phosphite complexes support the proposed structures. The carbonyl spectra are recorded in Table I. The acyl carbonyl absorption band moves to higher wave lengths as the number of phosphite ligands increases, the values being about 5.8, 5.9, 6.0 and 6.2 μ with zero, one, two and three phosphite groups coördinated in the acyl complex. The coördinated carbonyl bands show a similar trend.

The phosphorus n.m.r. spectra of the complexes were investigated in the hope of discovering the positions of the ligands in these presumably trigonal bipyramidal complexes. The bands were so weak and broad, however, that nothing could be concluded from the spectra.

The mechanism of the reaction of the alkylcobalt carbonyls or carbonyl phosphites with phosphites to form acylcobalt derivatives is of considerable interest. Originally we proposed a coördinately unsaturated acylcobalt species as an intermediate in the reaction.[7] The existence of this acylcobalt complex was based upon infrared evidence. Solutions of alkylcobalt tetracarbonyls prepared from alkyl halides and sodium cobalt carbonyl at 0° have acyl carbonyl bands in their infrared spectra at 5.8 μ. One explanation for this band which also was consistent with the reactions of these compounds was that the alkylcobalt tetracarbonyls were actually equilibrium mixtures of the alkyl tetracarbonyls and acylcobalt tricarbonyls.

$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3$$
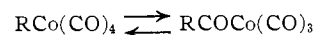
It now appears that the 5.8 μ band is, at least largely if not entirely, from acylcobalt tetracarbonyl, which is formed by some kind of a decomposition or disproportionation reaction taking place in the infrared cell or during the preparation of the compound.[8]

There is, however, at least one known example of a coördinately unsaturated monovalent cobalt carbonyl derivative which exists in equilibrium with a saturated species. This is π-allylcobalt dicarbonyl which is in equilibrium with the tricarbonyl.[9] The tricarbonyl reacts with triphenylphosphine to form the monophosphine derivative in a first-order reaction independent of the phosphine concentration. Since a coördinately unsaturated intermediate apparently exists in this reaction it is not unreasonable to expect a similar intermediate may exist in the alkylcobalt to acylcobalt reaction even though the concentration of the intermediate may be too low to measure by infrared methods. The following mechanism therefore still seems to be a reasonable one.[3,10]

$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3$$
$$RCOCo(CO)_3 + PR_3 \longrightarrow RCOCo(CO)_3PR_3$$
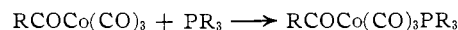
Another possible mechanism for this type of reaction has been proposed recently by Calderazzo and Cotton.[11] Their mechanism involves a second-order reaction between the alkylmetal carbonyl and the new entering ligand simultaneously causing a coördinated carbonyl to insert itself between the alkyl group and the metal.

$$RM(CO)_n + L \longrightarrow RCOM(CO)_{n-1}L$$
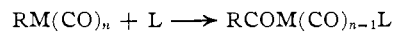
There is not enough information available at this time to decide between these two mechanisms.

(7) R. F. Heck and D. S. Breslow, Second Intern. Catalysis Congress, Paris, France, July 4–9, 1960, paper 27; Chem. Ind. (London), 467 (1960).
(8) G. Bor, personal communication.
(9) R. F. Heck, J. Am. Chem. Soc., 85, 655 (1963).
(10) R. F. Heck, ibid., 85, 651 (1963).
(11) F. Calderazzo and F. A. Cotton, Inorg. Chem., 1, 30 (1962).

Experimental

Yields of products were not quantitatively determined in some of the following experiments, mainly because of the inconvenience of weighing air-sensitive or unstable samples. In all experiments, the products obtained were the major ones formed and yields appeared to be good.

Acetylcobalt Dicarbonyl Trimethyl Phosphite Triphenylphosphine.—In a capped bottle fitted with a self-sealing rubber liner, at 0°, were placed 30 ml. of 0.1 M sodium cobalt tricarbonyl triphenylphosphine in tetrahydrofuran[4] and 0.5 ml. of methyl iodide. After about an hour at 0° the infrared spectrum showed that the 5.4 μ band of the cobalt tricarbonyl triphenylphosphine anion had disappeared and methylcobalt tricarbonyl triphenylphosphine had been formed. Then 6.0 ml. of 1.0 M trimethyl phosphite in ether was added. After 30 minutes at 0°, the solvent was evaporated to a few milliliters and the insoluble salts formed were removed by centrifuging. Addition of pentane to the solution caused crystallization of the product. Several more recrystallizations from warm ether gave yellow prisms of the complex, m.p. 105–106.5° dec.

Anal. Calcd. for $C_{25}H_{27}O_6P_2Co$: C, 55.15; H, 5.00. Found: C, 55.67; H, 5.37.

From the mother liquors of the recrystallization there was obtained a second product which was obtained as nearly colorless plates after several recrystallizations from pentane. The compound was acetylcobalt dicarbonyl bis-(trimethyl phosphite), m.p. 35°.

Anal. Calcd. for $C_{10}H_{21}O_9P_2Co$: C, 29.67; H, 5.21. Found: C, 30.17; H, 5.42.

Methoxyacetylcobalt dicarbonyl trimethyl phosphite triphenylphosphine was prepared exactly as the above acetyl compound was, 0.5 ml. of chloromethyl methyl ether being used in place of the methyl iodide. The product, after several recrystallizations from methylene chloride–ether, melted at 98.5–101° dec.

Anal. Calcd. for $C_{26}H_{29}O_7P_2Co$: C, 54.37; H, 5.09. Found: C, 54.63; H, 5.29.

Acetylcobalt Tricarbonyl Trimethyl Phosphite.—In a capped, nitrogen-filled bottle fitted with a self-sealing rubber liner, at 0°, were placed 100 ml. of 0.07 M sodium cobalt carbonyl in ether, 8.0 ml. of 1.0 M trimethyl phosphite in ether and 1.0 ml. of methyl iodide. After 1 hour at 0°, the infrared spectrum showed all the cobalt carbonyl anion had reacted (disappearance of the 5.4 μ band). Evaporation of the solvent at room temperature left an oil, which was crystallized from pentane at −80°. The compound appeared to be decomposing and depositing insoluble material as it was being purified. Satisfactory analyses could not be obtained. Nevertheless, it is clear from the infrared spectrum (Table I) that the compound was the expected one.

Acetylcobalt Dicarbonyl Bis-(Trimethyl Phosphite).—In a capped, nitrogen-filled bottle fitted with a self-sealing rubber liner, at 0°, were placed 100 ml. of 0.07 M sodium cobalt tetracarbonyl in ether, 4.0 g. of trimethyl phosphite and 3.0 ml. of methyl iodide. The solution was shaken and, after one hour at 0°, the solvent was evaporated to remove excess methyl iodide and 100 ml. of pentane was added. The mixture was heated to 70° in a hot water-bath for about one hour and cooled to room temperature. Insoluble salts were removed by centrifuging and the clear pentane solution was evaporated under vacuum to about 15 ml. On being cooled to −80° the product crystallized. After two more recrystallizations from pentane, 3.02 g. of pale yellow crystals was obtained, m.p. 35°, identical with the second compound obtained above from methylcobalt tricarbonyl triphenylphosphine and trimethyl phosphite.

Methylcobalt Dicarbonyl Bis-(Trimethyl Phosphite).—To a solution of 3.13 g. of acetylcobalt dicarbonyl bis-(trimethyl phosphite) in 6 ml. of tetrahydrofuran under nitrogen was added 8.0 ml. of 1.0 M sodium methoxide in methanol. After standing at room temperature overnight, the solution was evaporated to dryness under vacuum and the solid was washed twice with a one-to-one solution of ether and pentane. A slurry of the solid in 10 ml. of tetrahydrofuran was then treated with 1.0 ml. of methyl iodide. The solid rapidly dissolved, and it was necessary to cool the solution to keep it at room temperature. After about 15 minutes, the solution was evaporated to dryness, and the product was extracted from the residue with several small portions of ether. Insoluble sodium iodide was removed by centrifuging the solution. Concentration of the solution and addition of pentane followed by cooling led to the formation of pale yellow plates of methylcobalt dicarbonyl bis-(trimethyl phosphite). Three more recrystallizations from ether–pentane gave 1.6 g. of a sample, m.p. ~50°.

Anal. Calcd. for $C_9H_{21}O_8P_2Co$: C, 28.58; H, 5.60. Found: C, 28.71; H, 5.68.

Acetylcobalt Carbonyl Tris-(Trimethyl Phosphite).—A solution of 2.00 g. of methylcobalt dicarbonyl bis-(trimethyl phosphite) and 1.0 ml. of trimethyl phosphite in 10 ml. of pentane under nitrogen in a capped tube was heated to 75° in hot water for 15

minutes. After the solution was cooled, about 10 ml. of ether was added and the solution was left overnight at −80° to crystallize. The product which separated was recrystallized three more times from ether–pentane solution to give 0.5 g. of clusters of yellow prisms, m.p. 49–50°.

Anal. Calcd. for $C_{12}H_{30}O_{11}P_3Co$: C, 28.70; H, 6.02. Found: C, 28.90; H, 6.18.

Methylcobalt Tricarbonyl Trimethylolpropane Phosphite.—A solution of 5.0 g. of dicobalt octacarbonyl in 50 ml. of ether was mixed with a solution of 5.0 g. of trimethylolpropane phosphite in 10 ml. of ether under nitrogen. After about 10 minutes of shaking, the brown solid formed was separated and quickly air-dried. The compound, presumably dicobalt hexacarbonyl bis-(trimethylolpropane phosphite), turned dark on standing in the air for more than a few minutes. The material was then placed in a bottle containing 40 g. of 1% sodium amalgam and the bottle was capped with a metal cap with two holes in it and a self-sealing rubber liner. The bottle was flushed with nitrogen, 100 ml. of pure tetrahydrofuran was added and the mixture was shaken overnight to prepare a 0.1 M solution of sodium cobalt tricarbonyl trimethylolpropane phosphite.

In a nitrogen-filled tube at 0° were placed 10 ml. of the above 0.1 M sodium cobalt tricarbonyl (trimethylolpropane phosphite) solution in tetrahydrofuran and 0.5 ml. of methyl iodide. After 30 minutes at 0°, the infrared spectrum (Table I) showed that methylcobalt tricarbonyl trimethylolpropane phosphite had been formed. Evaporation of the solvent left an oil which gradually crystallized when it was stirred with pentane, but the compound decomposed on attempted purification at room temperature.

Acetylcobalt Tricarbonyl Trimethylolpropane Phosphite.—A solution of 60 ml. of 0.07 M sodium cobalt carbonyl in ether and 5.0 ml. of 1.0 M acetyl chloride in ether was allowed to react for about an hour at 0° under nitrogen. To the acetylcobalt tetracarbonyl solution so formed was added 5.5 ml. of 1.0 M trimethylolpropane phosphite in ether. After 30 minutes, the solution was centrifuged to remove the sodium chloride formed and evaporated to about 10 ml. Addition of an equal volume of pentane precipitated a brown oil. The clear supernatant solution was removed and on cooling it deposited large colorless plates of acetylcobalt tricarbonyl trimethylolpropane phosphite. Several recrystallizations from pentane, however, failed to give a completely pure product.

Anal. Calcd. for $C_{11}H_{14}O_7PCo$: C, 37.95; H, 4.05. Found: C, 38.53; H, 4.40.

Acetylcobalt Dicarbonyl Bis-(Trimethylolpropane Phosphite).—In a large bottle fitted with a self-sealing, rubber-lined cap, and filled with nitrogen, was placed 300 ml. of 0.07 M sodium cobalt carbonyl in ether. After the contents of the bottle were cooled to 0°, 1.6 ml. of pure acetyl chloride was added. The solution was mixed well and left at 0° overnight to form acetylcobalt tetracarbonyl. Then 45 ml. of 1.0 M trimethylolpropane phosphite in ether was added and the solution was allowed to warm up at room temperature during about 30 minutes. The gas formed was vented and the solution was heated for 1 hour in hot water at 75° with occasional venting of the gas formed. After the solution was cooled to room temperature, the solvent was again evaporated under vacuum and the solid residue was extracted with methylene chloride several times. The insoluble salts were removed by centrifuging and the solution was evaporated to about 20 ml. Addition of pentane caused the product to crystallize. Several recrystallizations from methylene chloride–ether or tetrahydrofuran–pentane at 0° gave the pure product as yellow-green crystals, m.p. 185° dec.

Anal. Calcd. for $C_{16}H_{25}O_9P_2Co$: C, 39.84; H, 5.22. Found: C, 40.37; H, 5.46.

Methylcobalt Dicarbonyl Bis-(Trimethylolpropane Phosphite).—To a solution of 1.93 g. of acetylcobalt dicarbonyl bis-(trimethylolpropane phosphite) in 10 ml. of tetrahydrofuran under nitrogen was added 4.0 ml. of 1.0 M sodium ethoxide in tetrahydrofuran solution. A clear green solution was formed which soon began to deposit crystals of sodium cobalt dicarbonyl bis-(trimethylolpropane phosphite). After about an hour at room temperature, the solid was separated by centrifuging and the solution was discarded. The solid was washed twice more with 5-ml. portions of tetrahydrofuran. A slurry of the sodium salt in 5 ml. of tetrahydrofuran under nitrogen was cooled to 0° and 0.5 ml. of methyl iodide was added. The solid dissolved in a few minutes and soon the product began to crystallize. Addition of 5 ml. of pentane and cooling to 0° precipitated all of the product. The solid obtained was separated and extracted with methylene chloride. The insoluble sodium iodide was removed by centrifuging and addition of ether to the methylene chloride solution caused the methylcobalt dicarbonyl bis-(trimethylolpropane phosphite) to crystallize out. There was obtained 0.81 g. of pale yellow prisms, m.p. 185–200° dec. An analytical sample was prepared by recrystallizing a portion of the product three more times from methylene chloride–pentane.

Anal. Calcd. for $C_{15}H_{25}O_8P_2Co$: C, 39.65; H, 5.55. Found: C, 39.77; H, 4.96.

Acetylcobalt Carbonyl Tris-(Trimethylolpropane Phosphite).—A solution of 0.81 g. of methylcobalt carbonyl bis-(trimethylolpropane phosphite) in 5 ml. of methylene chloride was treated with 2.0 ml. of 1.0 M trimethylolpropane phosphite in ether. After 30 minutes at room temperature, the solution was evaporated to 3 or 4 ml. and 5 ml. of ether was added. The product immediately crystallized as clusters of fine colorless needles. Two more recrystallizations from methylene chloride–ether gave 0.65 g. of acetylcobalt carbonyl tris-(trimethylolpropane phosphite). The complex had no definite melting point but decomposed gradually as it was heated.

Anal. Calcd. for $C_{21}H_{36}O_{11}P_3Co$: C, 40.92; H, 5.89. Found: C, 40.96; H, 5.90.

Methylcobalt Carbonyl Tris-(Trimethylolpropane Phosphite).—A solution of 0.60 g. of acetylcobalt tris-(trimethylolpropane phosphite) in tetrahydrofuran (not all dissolved) was mixed with 1.0 ml. of 1.0 M sodium ethoxide in tetrahydrofuran under nitrogen. The mixture was shaken for about an hour and then the insoluble sodium cobalt carbonyl tris-(trimethylolpropane phosphite) formed was separated by centrifuging and washed with two 5-ml. portions of fresh tetrahydrofuran. Then, to a slurry of this sodium salt in 5 ml. of tetrahydrofuran, 0.5 ml. of methyl iodide was added at 0° under nitrogen. The mixture was allowed to warm up slowly, and in 30 minutes nearly all the solid had dissolved. Evaporation of the solution left an oil and sodium iodide. The oil was separated by extraction with methylene chloride. Evaporation of the extracts to a few milliliters followed by the addition of ether gave crystals of the product. Several more crystallizations from methylene chloride–ether gave a nearly colorless powder, m.p. ~185° dec.

Anal. Calcd. for $C_{20}H_{36}O_{10}P_3Co$: C, 40.85; H, 6.17. Found: C, 40.73; H, 6.19.

This compound did not react with more trimethylolpropane phosphite in methylene chloride even on heating to 100°.

Cobalt Dicarbonyl Bis-(Trimethylolpropane Phosphite) Hydride.—A solution of 0.95 g. of acetylcobalt dicarbonyl bis-(trimethylolpropane phosphite) in 30 ml. of tetrahydrofuran was placed in a 110-ml. hydrogenation vessel and pressured to 3000 p.s.i. with hydrogen. The solution was heated to 60° and rocked for 12 hours. After cooling, the excess hydrogen was vented and the clear brown reaction mixture was removed by

means of a hypodermic syringe to protect the product from the air. Evaporation of the solution under vacuum at room temperature left a tan solid. The product was taken up in methylene chloride and pentane was added dropwise until a black amorphous material separated. The solution was centrifuged to remove the black material and, on cooling, tan crystals of the hydride were obtained. Several recrystallizations from methylene chloride–pentane gave a sample, m.p. 155–160° dec.

Anal. Calcd. for $C_{14}H_{23}O_8P_2Co$: C, 38.20; H, 5.27. Found: C, 38.58; H, 5.40.

Acetylcobalt Tricarbonyl Tris-(p-anisyl)-phosphine.—A solution of 0.34 g. of dicobalt octacarbonyl in 5 ml. of methylene chloride at 0° was treated with a solution of 0.8 g. of tris-(p-anisyl)phosphine (prepared from p-anisylmagnesium bromide and phosphorus trichloride) in 5 ml. of methylene chloride. Evaporation of the solution after an hour left a dark oil which was probably bis-[tris-(p-anisyl)phosphine] cobalt tricarbonyl cobalt tetracarbonylate. The oil was diluted with 5.0 ml. of ether in a capped tube and heated at about 100° for an hour to convert the compound into the tri-p-anisylphosphine cobalt tricarbonyl dimer. The ether-insoluble solid brown dimer was filtered off and air-dried. There was obtained 0.74 g. of product.

Sodium cobalt tricarbonyl tris-(p-anisyl)-phosphine was prepared by shaking 0.74 g. of the above dimer with 12 ml. of tetrahydrofuran and 5.0 g. of 1% sodium amalgam in a capped tube under nitrogen overnight. The solution was centrifuged and the clear ~0.1 M solution of the sodium salt was transferred to another nitrogen-filled tube, where it was cooled to 0° and 0.5 ml. of methyl iodide was added. After an hour at 0°, the infrared spectrum showed that methylcobalt tricarbonyl tris-(p-anisyl)phosphine had been formed (bands at 4.91 (w) μ and 5.10 (vs) μ. An attempt was made to measure the rate of uptake of carbon monoxide by this compound at 0° under one atmosphere of pressure, but the reaction was much too fast under these conditions. From the reaction mixture, by evaporation and recrystallization several times from methylene chloride–pentane, a good yield of acetylcobalt tricarbonyl tris-(p-anisyl)-phosphine, as yellow prisms, m.p. 125–126° dec., was obtained.

Anal. Calcd. for $C_{26}H_{24}O_7PCo$: C, 58.00; H, 4.49. Found: C, 58.35; H, 4.90.

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Carbonate Ligand and Hydrogen Exchange Studies of Some Carbonatoamine Cobalt(III) Complex Ions: A General Mechanism for the Ligand Carbonate Exchange Reaction in Aqueous Solution

BY GABRIEL LAPIDUS[1] AND GORDON M. HARRIS

Several studies have been made in recent years of the carbonate substitution reactions in aqueous solution of carbonatocobalt(III) complex ions of the general type Co L CO_3^-, where L represents an amine ligand grouping. This paper reports the results of a detailed study of the kinetics of the carbonate exchange reactions of $Co(pn)_2CO_3^+$ (pn = propylenediamine), and includes a complete reassessment of earlier data on the reactions of the analogs in which the group L is pentaammine (N_5), tetraammine (N_4), ethylenediamine (en$_2$), cis-diamminoethylenediamine (N_2en), and trimethylenediamine (tn$_2$). New data on the acidity dependence of the reactions has confirmed that the whole series react by a common dual mechanism involving both second-order carbonate/carbonato exchange and pseudo-first-order aquation. The rate law is of the form: $R = k'\alpha\beta ab + k''\alpha a$, where a and b are the total concentrations of complex and free carbonate, respectively, and α and β are functions of the form $Kh/Kh + 1$, with h = hydrogen ion concentration, and K a protonation equilibrium constant. Much of the variation in reactivity between members of the series appears to be of stereochemical origin, in which intramolecular O–H–N hydrogen-bonding may play a significant role. Evidence concerning this latter factor has been adduced from rate studies of the deuterium exchange between the amine hydrogens of several of these complexes and the solvent water. An important conclusion from the study is that it is only a protonated species, whether of complexed or free carbonate, which takes part in the reactions at an appreciable rate.

The exchange reaction in aqueous solution between free (uncomplexed) carbonate ion and the corresponding ligand group in various monocarbonatoaminecobalt(III) complex ions has been the subject of a number of investigations.[2-6] Since the complexes

studied all have the same total charge and an identical central metal ion, unequivocal evidence is provided concerning the effect of different but related uncharged substitution-inert ligands on the kinetics of the displacement reactions of the adjacent dibasic carbonato ligand. The preceding paper in our own series[2] dealt

(1) Work done as part of Ph.D. requirement of University of Buffalo, 1961; complete report available from University Microfilms, Ann Arbor, Mich.

(2) J. E. Boyle and G. M. Harris, *J. Am. Chem. Soc.*, **80**, 782 (1958).

(3) (a) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952); (b) D. R. Stranks, *ibid.*, **48**, 911 (1952).

(4) D. R. Stranks, *ibid.*, **51**, 505 (1955).

(5) J. S. Holden and G. M. Harris, *J. Am. Chem. Soc.*, **77**, 1934 (1955).

(6) R. A. W. Pratt, E. Sherwin and G. J. Weston, *J. Chem. Soc.*, 476 (1962).