IV

V

VI

VII

a much more favorable situation than for the divalent metal ions. On the basis of the *a priori* reasoning given above for the low stabilities of the chelates of divalent metal ion, this is not an unreasonable result. Therefore it seems that the ligands of the type described in this paper may have exceptionally high affinities for metal ions of +4 charge. In order to investigate this idea, work on the synthesis and thermodynamic study of these and similar ligands is being continued in these laboratories.

The combination of Cu(II) and ENTMP, with the displacement of two additional protons over that occurring with the free ligand at the same pH, suggests structure VI for the initial metal–ligand bonding. Four subsequent proton dissociation steps, indicated by the potentiometric curves, suggest increasing engagement of the phosphonate oxygen atoms as indicated by VII. This process leads ultimately to the Cu(II) chelate of the completely dissociated ligand, shown clearly by the potentiometric curve. This compound probably involves tetragonal (hexadentate) coordination of the Cu(II) ion.

Steric and Electronic Effects in the Dissociation of Cobalt Carbonyl Derivatives. IV. Rates of Dissociation of Mono(trimethylolpropane phosphite) Derivatives and π-Allylcobalt Carbonyl Bis(trimethylolpropane phosphite) Complexes

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π-Allylcobalt tricarbonyl complexes react with 2 moles of trimethylolpropane phosphite to produce π-allylcobalt carbonyl bis(trimethylolpropane phosphite) derivatives. Cobalt hydrocarbonyl reacts similarly producing cobalt hydrodicarbonyl bis(trimethylolpropane phosphite). The kinetics of replacement of carbon monoxide in these complexes and the related acetylcobalt carbonyl complexes have been studied. All appear to react by first-order dissociation mechanisms.
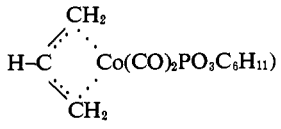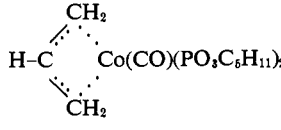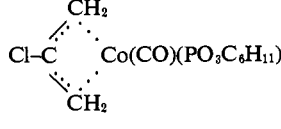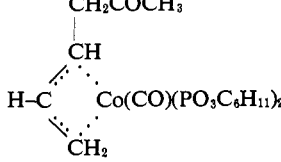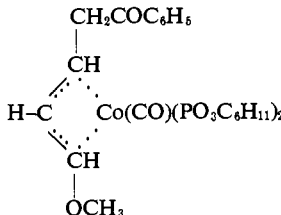
Introduction

Phosphite esters successively replace two coordinated carbon monoxide groups from acylcobalt tetracarbonyls.[1] The mechanism of replacement of the first carbon monoxide has been shown to involve a first-order dissociation process.[2] The mechanism of replacement of the second carbon monoxide has now been studied to determine the influence of the phosphite group upon the second replacement reaction. A similar replacement of two coordinated carbon monoxide groups by phosphite esters has also been found to take place with π-allylcobalt tricarbonyl complexes. The kinetics of these replacement reactions are reported in this paper along with several examples of the preparation of π-allylcobalt carbonyl bis(phosphite) complexes. Cobalt hydrotricarbonyl trimethylolpropane phosphite also reacted with a second mole of trimethylolpropane phosphite. The mechanism of this

(1) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1220 (1963).

(2) R. F. Heck, *ibid.*, **85**, 651 (1963).

Table I. Trimethylolpropane Phosphite Derivatives of Cobalt Carbonyl Complexes

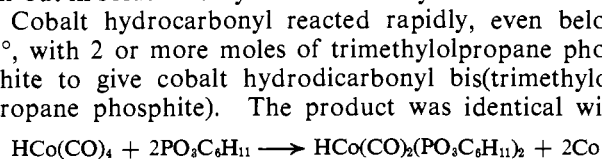| Compound	M.p., °C.	Color	ν_{CO}, cm.$^{-1}$ [a]	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
CH₂ / H–C ⟨ ⟩ Co(CO)₂PO₃C₆H₁₁) \ CH₂	107–112 dec.	Yellow-orange needles	1965 (vs) 2025 (vs) 2070 (w)	C₁₁H₁₆O₅PCo	41.52	5.07	41.62	5.26
CH₂ / H–C ⟨ ⟩ Co(CO)(PO₃C₆H₁₁)₂ \ CH₂	230–232 dec.	Yellow plates	1965 (vs)	C₁₆H₂₇O₇P₂Co	42.49	6.02	42.23	5.98
CH₂ / Cl–C ⟨ ⟩ Co(CO)(PO₃C₆H₁₁)₂ \ CH₂	155–157 dec.	Yellow prisms	1980 (s)	C₁₆H₂₆O₇PClCo	39.48	5.39	39.20	5.48
CH₂COCH₃ | CH / H–C ⟨ ⟩ Co(CO)(PO₃C₆H₁₁)₂ \ CH₂	172–173 dec.	Orange powder	1970 (vs) 1660 (s)	C₁₉H₃₁O₈P₂Co	44.89	6.15	44.12	6.51
CH₂COC₆H₅ | CH / H–C ⟨ ⟩ Co(CO)(PO₃C₆H₁₁)₂·OC₄H₈ \ CH | OCH₃	145–147 dec.	Yellow prisms	1685 (s) 1965 (vs)	C₂₉H₄₃O₁₀P₂Co	51.79	6.44[b]	51.55	6.69

[a] In CHCl₃. [b] Calcd.: P, 9.2. Found: P, 9.0.

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reaction has important implications in the catalytic chemistry of cobalt hydrocarbonyl.

Results

π-Allylcobalt carbonyl bis(trimethylolpropane phosphite) derivatives were obtained, in moderate yields, by heating π-allylcobalt tricarbonyls to about 75° in ether solutions in closed vessels with 2 or more moles of the phosphite ester. Bis(trimethylolpropane phos-

$$\pi\text{-}C_3H_5Co(CO)_3 + 2PO_3C_6H_{11} \longrightarrow$$
$$\pi\text{-}C_3H_5Co(CO)(PO_3C_6H_{11})_2 + 2CO$$

phite) derivatives were prepared from π-allyl-, 2-chloro-π-allyl-, 1-acetylmethyl-π-allyl-,[3] and 1-benzoyl-methyl-3-methoxy-π-allylcobalt tricarbonyls. All of the products were crystalline, yellow to orange solids. The crystalline compounds were reasonably stable in air but in solution they oxidized slowly in air.

Cobalt hydrocarbonyl reacted rapidly, even below 0°, with 2 or more moles of trimethylolpropane phosphite to give cobalt hydrodicarbonyl bis(trimethylolpropane phosphite). The product was identical with

$$HCo(CO)_4 + 2PO_3C_6H_{11} \longrightarrow HCo(CO)_2(PO_3C_6H_{11})_2 + 2Co$$

the sample prepared earlier by a different method.[1]

The new compounds prepared in this work are listed in Table I.

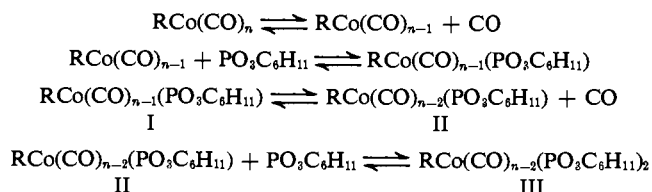It is a curious fact that triphenylphosphine will replace only one coordinated carbon monoxide in these complexes, whereas the phosphite esters easily replace two.

A study of the rates of replacement of the first and second carbonyl groups of various cobalt carbonyl derivatives by trimethylolpropane phosphite has provided useful information concerning the effect on the dissociation rates of substituents on the metal.

All of the reactions appeared to be first order in the cobalt complexes and zero order in phosphite ester, at least under the conditions used. The reactions were followed by measuring the rate of gas evolution, using the experimental infinity values for calculating the rate constants. The data obtained are summarized in Table II. The kinetics are consistent with first-order dissociation reactions as the rate-determining steps.

$$RCo(CO)_n \rightleftharpoons RCo(CO)_{n-1} + CO$$

$$RCo(CO)_{n-1} + PO_3C_6H_{11} \rightleftharpoons RCo(CO)_{n-1}(PO_3C_6H_{11})$$

$$\underset{I}{RCo(CO)_{n-1}(PO_3C_6H_{11})} \rightleftharpoons \underset{II}{RCo(CO)_{n-2}(PO_3C_6H_{11})} + CO$$

$$\underset{II}{RCo(CO)_{n-2}(PO_3C_6H_{11})} + PO_3C_6H_{11} \rightleftharpoons \underset{III}{RCo(CO)_{n-2}(PO_3C_6H_{11})_2}$$

The dissociation rates of acylcobalt tetracarbonyls[2] and π-allylcobalt tricarbonyls have been discussed elsewhere.[4] The dissociation rates of the monotrimethylolpropane phosphite derivatives of these complexes seem to be completely analogous except that the equilibria are not as far toward the bisphosphite

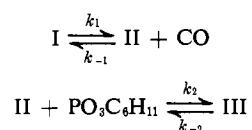(3) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3381 (1963).

(4) R. F. Heck, *ibid.*, **85**, 655 (1963).

Table II. Rates of Reaction of Trimethylolpropane Phosphite with Various Cobalt Carbonyl Complexes in Diglyme Solution

Compound	Concn., M	$PO_3C_6H_{11}$ concn.,[a] M	Temp., °C.	Rate constant, sec.$^{-1}$	ΔE^*	ΔS^*
$CH_3COCo(CO)_4$	0.066	0.231	0.0	$5.55 \pm 0.30 \times 10^{-4}$		
	0.057	0.231	25.0	$1.84 \pm 0.08 \times 10^{-2}$		
	0.045	0.375	25.0	$1.33 \pm 0.04 \times 10^{-2}$	20.5	−0.2
$CH_3COCo(CO)_3(PO_3C_6H_{11})$	0.072	1.125	25.0	$4.00 \pm 0.08 \times 10^{-5}$		
	0.072	2.500	25.0	$3.50 \pm 0.20 \times 10^{-5}$		
	0.071	0.286	50.1	$1.22 \pm 0.03 \times 10^{-3}$		
	0.076	0.900	50.1	$1.22 \pm 0.02 \times 10^{-3}$	24.9	3.4
	0.063	0.375	70.1	$1.26 \pm 0.04 \times 10^{-2}$		
	0.068	1.125	70.1	$1.18 \pm 0.02 \times 10^{-2}$		
$\pi\text{-}C_3H_5Co(CO)_3$	0.068	0.286	0.0	$2.19 \pm 0.06 \times 10^{-4}$		
	0.069	0.286	25.3	$9.76 \pm 0.14 \times 10^{-3}$	23.7	2.2
	0.061	0.333[c]	25.0	$8.49 \pm 0.13 \times 10^{-3}$		
$\pi\text{-}C_3H_5Co(CO)_2(PO_3C_6H_{11})$	...	...	25.0	7.89×10^{-6} [b]		
	0.077	0.231	49.9	$4.24 \pm 0.08 \times 10^{-4}$		
	0.089	1.636	50.1	$2.73 \pm 0.06 \times 10^{-4}$	27.0	6.7
	0.077	0.231	75.0	$7.55 \pm 0.16 \times 10^{-3}$		
	0.048	1.421	74.9	$6.16 \pm 0.15 \times 10^{-3}$		
	0.066	2.308	74.8	$5.83 \pm 0.16 \times 10^{-3}$		
$HCo(CO)_3(PO_3C_6H_{11})$	0.055	0.059	−25.0	$1.34 \pm 0.09 \times 10^{-2}$		
	0.059	0.128	−24.5	$1.72 \pm 0.06 \times 10^{-2}$		

[a] Trimethylolpropane phosphite concentration. [b] Extrapolated value. [c] Concentration of triphenylphosphine.

derivative as they were toward the monophosphite complex. Infrared evidence indicated that small amounts of the monophosphite derivatives were present in equilibrium with the bisphosphite derivatives. The reverse reaction was apparently essentially completely suppressed, judging by infrared spectra, by increasing the phosphite ester concentration to 1.5 to 2.5 M. Apparently the equilibrium is far enough toward the bisphosphite product that under the conditions used the kinetics were not much affected by the changes in the phosphite concentration. The slight decreases observed on increasing the phosphite concentration could be the result of medium changes or because the experimental rather than the theoretical infinity values were used in the rate constant calculations. The kinetic expression for the second dissociation reaction then is

$$I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} II + CO$$

$$II + PO_3C_6H_{11} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} III$$

$$\frac{d(I)}{dt} = -\frac{d(CO)}{dt} =$$

$$k_1[I] - \frac{k_1k_{-1}[I][CO] + k_{-1}k_{-2}[III][CO]}{k_{-1}[CO] + k_2[PO_2C_6H_{11}]}$$

From this expression it is clear that as $[PO_3C_6H_{11}]$ is increased, the second term becomes smaller and the rate approaches the value of $k_1[I]$.

The fact that cobalt hydrotricarbonyl trimethylolpropane phosphite undergoes a first-order dissociation probably has some bearing upon the reactions of cobalt hydrocarbonyl itself. The latter compound is much too reactive toward phosphines[5] for us to be able to measure kinetics by our techniques, but since the acylcobalt carbonyls and the π-allylcobalt tricarbonyls react by the same first-order mechanism after they are

(5) R. F. Heck, J. Am. Chem. Soc., 85, 657 (1963).

substituted with phosphite ester groups, it is reasonable to expect that cobalt hydrocarbonyl does also. This evidence supports our previous contention that not cobalt hydrocarbonyl, but the dissociated form, cobalt hydrotricarbonyl, is the reactive species in the oxo and related reactions.[6]

It is instructive to note the effect of substituents upon the ease of dissociation of the cobalt complexes. The presence of one trimethylolpropane phosphite group in acetylcobalt tricarbonyl trimethylolpropane phosphite decreases the rate of dissociation by a factor of about 380 at 25° while in a similar comparison in the π-allylcobalt tricarbonyl series, the factor is about 1080. Cobalt hydrotricarbonyl trimethylolpropane phosphite dissociates some 10^6 times more rapidly than acetylcobalt tricarbonyl trimethylolpropane phosphite does. Such a large effect may be caused by a *trans* effect of hydrogen upon a carbonyl group, presumably both in the apical positions of a distorted trigonal bipyramid, although there is little evidence to support this conclusion at the present time.

Experimental

π-*Allylcobalt Dicarbonyl Trimethylolpropane Phosphite.* Into a nitrogen-filled bottle, which had been capped with a self-sealing rubber-lined metal cap with two small holes in it for "hypodermic injection," were injected 60 ml. of 0.07 M NaCo(CO)$_4$[7] in ether and 5.0 ml. of 1.0 M allyl chloride in ether. The solution was heated for 1 hr. in a water bath at about 75°. The solution was cooled to room temperature and 5.0 ml. of 1.0 M trimethylolpropane phosphite[8] in ether was added. After an hour at room temperature, the solution was centrifuged to remove the sodium bromide formed and evaporated *in vacuo* at room

(6) R. F. Heck and D. S. Breslow, ibid., 83, 4023 (1961).

(7) W. Hieber, O. Vohler, and G. Braun, Z. Naturforsch., 13b, 192 (1958).

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

temperature. The crystalline residue was recrystallized under nitrogen three times by dissolving it in 4 ml. of methylene chloride, adding 5 ml. of pentane, and cooling to −5°. There was obtained 0.55 g. of yellow-orange needles with the properties shown in Table I.

π-Allylcobalt Carbonyl Bis(trimethylolpropane phosphite). An ether solution of π-allylcobalt tricarbonyl was prepared from 30 ml. of 0.07 *M* NaCo(CO)₄[7] in ether and 2.5 ml. of 1.0 *M* allyl chloride in ether by heating the solutions together under nitrogen in a capped bottle at about 75° for an hour as described in the previous experiment. The carbon monoxide produced was vented from the bottle and 5.0 ml. of 1.0 *M* trimethylolpropene phosphite[8] in ether was added. The gas formed was vented again and the solution was heated to 75° for another hour. Yellow crystals of the product separated from the solution during this time. After cooling, the reaction mixture was diluted with 20 ml. of pentane and cooled in Dry Ice, and the solid formed was separated by centrifuging. The product was separated from inorganic salts by extracting it with methylene chloride, all operations being carried out under nitrogen. Filtration or centrifuging the extracts, concentrating to about 4 or 5 ml., and adding 10 ml. of ether caused the product to crystallize after cooling to 0°. Another recrystallization in the same manner gave 0.50 g. of product in the form of bright yellow plates with the properties shown in Table I.

2-Chloro-π-allylcobalt Carbonyl Bis(trimethylolpropane phosphite). Into a capped, nitrogen-filled bottle as used above were injected 30 ml. of 0.07 *M* NaCo(CO)₄[7] in ether and 2.5 ml. of 1.0 *M* 2,3-dichloropropene in ether. The solution was heated to 75° for an hour and the carbon monoxide formed was vented. Then 5.0 ml. of 1.0 *M* trimethylolpropane phosphite[8] in ether was added and heating was continued for another hour at about 75°. A mixture of yellow crystals of the product and black crystals of cobalt tricarbonyl separated during the heating. The solution was evaporated at room temperature and the product was taken up in methylene chloride. After centrifuging, pentane was slowly added. The black material which precipitated was separated by centrifuging and the solution was cooled in Dry Ice. The yellow crystals which now formed were isolated and recrystallized by dissolving in a minimum of ether and adding an equal volume of pentane and cooling in Dry Ice. About 0.1 g. of yellow powder with the properties shown in Table I was isolated.

1-Acetylmethyl-π-allylcobalt Carbonyl Bis(trimethylolpropane phosphite). Into a nitrogen-filled, capped bottle as used in the above experiments was injected 30 ml. of 0.07 *M* NaCo(CO)₄[7] in ether, 2.5 ml. of 1,3-butadiene, and 0.5 ml. of methyl iodide.[3] The solution was let stand an hour at room temperature, and then 5.0 ml. of 1.0 *M* trimethylolpropane phosphite[8] in ether was added. The carbon monoxide formed was vented and the reaction solution was heated in a water bath at about 75° for an hour. On cooling, 20 ml. of pentane was added and the solution was let

stand overnight at −5°. The orange crystals formed were separated and recrystallized twice by dissolving them in a minimum of methylene chloride, filtering the first time to remove sodium iodide, and then adding twice the volume of ether and cooling to −5°. There was obtained 0.25 g. of orange powder with the properties shown in Table I.

1-Benzoylmethyl-3-methoxy-π-allylcobalt Carbonyl Bis(trimethylolpropane phosphite). A solution made up of 30 ml. of 0.07 *M* NaCo(CO)₄[7] in ether, 2.0 ml. of 1-methoxybutadiene, and 2.5 ml. of 1.0 *M* benzoyl chloride in ether, in a capped, nitrogen-filled bottle, was heated for about an hour at 50°. Then 5.0 ml. of 1.0 *M* trimethylolpropane phosphite[8] in ether was added and this solution was heated for about an hour at about 75°. The solution was then cooled and evaporated at room temperature. The residue was extracted with methylene chloride, centrifuged, and concentrated. The addition of pentane to the yellow oil obtained, followed by cooling, gave yellow crystals of the product. Two recrystallizations by dissolving the crystals in a minimum of tetrahydrofuran, adding an equal volume of pentane, and cooling to 0° gave 0.2 g. of pure product with the properties listed in Table I.

Cobalt Hydrotricarbonyl Trimethylolpropane Phosphite. To 28 ml. of 0.35 *M* HCo(CO)₄ in pentane[9] in a capped, nitrogen-filled bottle, cooled in a Dry Ice–acetone bath, was added 9 ml. of 1.0 *M* trimethylolpropane phosphite[8] in ether. The gas formed was vented and the colorless solid produced was separated by centrifuging at −20°. The product was quite unstable and had to be kept below 0°. It decomposed in a few hours at room temperature and also rapidly in air. The compound was too unstable to be analyzed.

Cobalt Hydrodicarbonyl Bis(trimethylolpropane phosphite). To 10 ml. of 0.18 *M* HCo(CO)₄ in pentane[9] at 0° (or below) was added 4.0 ml. of 1.0 *M* trimethylolpropane phosphite[8] in ether. The solution was diluted with 5 ml. of ether and then cooled in a Dry Ice–acetone bath. The tan solid present was separated by centrifuging and recrystallized twice by dissolving it in a minimum of methylene chloride, adding pentane, and cooling. There was obtained 0.05 g. of product, m.p. 255–260°, with infrared bands at 1960, 1990, and 2040 cm.⁻¹.

Acetylcobalt Tetracarbonyl and Tricarbonyl Trimethylolpropane Phosphite. The preparation of these compounds has been described elsewhere.[1]

π-Allylcobalt Tricarbonyl. This complex[10] was prepared by heating 30 ml. of 0.07 *M* NaCo(CO)₄[7] in ether with 2.5 ml. of 1.0 *M* allyl chloride in ether in a closed, nitrogen-filled bottle at 75° for an hour, and used without further purification.

Kinetic Measurements. The kinetics were measured by following the gas evolution. The techniques used have been described elsewhere.[2]

(9) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, 75, 2717 (1953).
(10) R. F. Heck and D. S. Breslow, *ibid.*, 83, 1097 (1961).