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DICARBONYL(TRIBUTYLPHOSPHINE)-π-CROTYLCOBALT: STRUCTURE AND REACTIVITY UNDER HYDROFORMYLATION CONDITIONS

W. W. SPOONCER, A. C. JONES AND L. H. SLAUGH
Shell Development Company, Emeryville, California 94608 (U.S.A.)

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SUMMARY

The complex, dicarbonyl(tri-n-butylphosphine)-π-crotylcobalt, (I), recently described by Mertzweiller and Tenney[1] as a hydroformylation catalyst, is unstable under hydroformylation conditions. It is rapidly converted, in the main, to butenes, butane, valeraldehydes, and the previously reported[2,3] active hydroformylation catalyst, bis[(tri-n-butylphosphine)tricarbonylcobalt], (II). Other products include tricarbonyl-π-crotylcobalt, (tributylphosphine)heptacarbonyldicobalt, butadiene, and amyl alcohols. At temperatures and pressures (*e.g.*, 110° and 500 psig of synthesis gas) where hydroformylation of 1-heptene occurs to an extent not exceeding 1% over a period of five hours, the complex (II) is always present when hydroformylation is first observed. At higher temperatures, the conversion rate for (I)→(II) is much higher; hydroformylation of 1-heptene proceeds in a similar manner to that which occurs when pure (II) is the initially added complex. It is not possible, therefore, that the complex (I) is the catalytic species responsible for hydroformylation. It is reasonable that the complex (II) promotes hydroformylation in the present instances.

Recently, Mertzweiller and Tenney[1] have described a metal complex, dicarbonyl(tributylphosphine)-2-butenylcobalt (I) purportedly capable of lowering the pressures required in the hydroformylation reaction. As part of our continuing study of hydroformylation chemistry[2,3], we have investigated the detailed structure of this interesting complex and studied its chemistry under hydroformylation conditions.

STRUCTURE OF (I)

The complex (I) was prepared by the method of Mertzweiller and Tenney from the reaction of tricarbonyl-π-crotylcobalt with tri-*n*-butylphosphine. The crude catalyst preparations contained 50-65% (I) which was separated and purified by elution chromatography.

Mertzweiller and Tenney cite as structural evidence for (I), only infrared metal carbonyl stretching frequencies measured on crude reaction products and a relative carbon monoxide content of crude products before and after treatment with tributylphosphine. We have obtained additional evidence relating to its structure.

Elemental analysis of chromatographed (I) indicated a complex $C_{18}H_{34}CoO_2P$. This material had an ebullioscopic molecular weight in benzene of 390±20 indicating a monomeric structure in solution. Its high resolution mass spectrum showed an ion with nominal mass 372 (nothing higher was detected). A fragment ion, resulting from CO loss from the parent ion had *m/e* 344 and an exact mass corresponding to a molecular formula $C_{17}H_{34}CoPO$. These, and other fragment ions whose exact masses were measured, are all consistent with the parent ion, *m/e* 372, having the empirical formula indicated.

The NMR spectrum of (I) at 100 MHz was measured in C_6D_6. The large proton resonances of the tributylphosphine ligand obscure a portion of the spectrum of the butenyl group near $\delta_H = 0.9$ and 1.4 ppm. When the phosphorus nuclei were decoupled by irradiation at $\delta_P = -41$ ppm, a four-line spectrum centered at 2.17 ppm collapsed to a single doublet, a multiplet centered at 2.60 ppm was simplified and a six-line spectrum centered at 4.42 ppm remained unchanged, indicating little, if any, coupling to the proton responsible for that resonance. For comparison, the spectrum of the triphenylphosphine analog, prepared by a modification of Heck and Breslow's method[4], was measured. The methyl resonance of the butenyl unit, centered at 1.41 ppm, consisted of four lines which collapsed to a doublet upon phosphorus decoupling. The resonances for each of the single protons centered at 1.65 and 2.06 ppm consisted of two doublets which collapsed to singlets upon phosphorus decoupling. A multiplet from the single proton resonance centered at 4.21 ppm was sharpened, but the basic six-line spectrum was little perturbed. The spectra of the two complexes are quite similar for the resonances in the butenyl proton region; first order analyses of the spectra yield the parameters listed in Table 1. The chemical shifts, and more diagnostically, the coupling constants for both complexes, clearly delineate π-crotyl systems (see, for example, ref. 5) present in the *syn* form of the complexes*. Thus (I) and its triphenylphosphine analog have the detailed structure indicated.

TABLE 1

NMR PARAMETERS FOR THE COMPLEXES π-$C_4H_7Co(CO)_2PR_3$

Chemical shift (δ)			Coupling constants, *J* (Hz)		
Of	$R=C_6H_5$	$R=n\text{-}C_4H_9$	Between	$R=C_6H_5$	$R=n\text{-}C_4H_9$
CH_3[a]	1.41	1.57	H_aH_d	10.1	10.4
H_a	1.65	1.35	H_bH_d	6.0	6.2
H_b	2.06	2.17	H_cH_d	9.5	9.0
H_c	2.72	2.60	H_cCCH_3	6.0	6.0
H_d	4.21	4.42	PH_a	2.0	—
P[b]	−64	−41	PH_b	9.7	9.5
			PH_c	*ca.* 0	2.9
			PCH_3	4.5	4.0

[a] In ppm from hexamethyldisiloxane. [b] In ppm from trimethyl phosphate.

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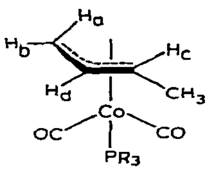
* The *syn* and *anti* nomenclature suggested by McClellan and coworkers[6] for the two forms of tricarbonyl-π-crotylcobalt (III) refers to the relative position of H_d and the methyl group. These workers and later, Bertrand and coworkers[7] concluded from NMR studies that the tricarbonyl existed as a mixture of *syn* and *anti* forms.



(I), $R = n\text{-}C_4H_9$

The infrared spectra of hexane solutions of (I) and its triphenylphosphine analog were observed in the carbonyl region with a resolution of 3 cm^{-1}. The spectral data, along with those of other complexes studied in this work, are recorded in Table 2.

TABLE 2

CARBONYL STRETCHING FREQUENCIES FOR COBALT COMPLEXES

Compound	Band position (cm^{-1})	$a \times 10^{-3}$ ($l \cdot mole^{-1} \cdot cm^{-1}$) in hexane	Compound	Band position (cm^{-1})	$a \times 10^{-3}$ ($l \cdot mole^{-1} \cdot cm^{-1}$) in hexane
$\pi\text{-}C_4H_7Co(CO)_2PBu_3$	1994	0.30	$[Co(CO)_3PBu_3]_2$	2030	—
(I)	1980[a]	2.2	(II)	1968	1.8
	1941	0.30		1950[a]	18.0
	1925	4.0		1925	0.8
	1894	0.09			
$\pi\text{-}C_4H_7Co(CO)_2PPh_3$	2001	0.44	$Bu_3PCo(CO)_3\text{-}Co(CO)_4$	2078[a]	3.2
	1991	2.3	(IV)	2021	3.7
	1950	0.25		1993	8.2
	1940	3.2		1958	1.6
	1906	0.05		1951	1.7
$\pi\text{-}C_4H_7Co(CO)_3$	2060[a]	3.0	$HCo(CO)_3PBu_3$	2045[a]	0.37
(III)	1993[a]	8.4		1968[a]	3.5

[a] Frequencies used for analyses during the controlled reactions of (I).

Because of the low symmetry of (I) and its triphenylphosphine analog, both carbonyl stretching modes absorb in the infrared spectrum. These are the strong bands at 1980 and 1925 cm^{-1} for the tributylphosphine derivative and 1991 and 1940 cm^{-1} for the triphenylphosphine derivative. The positions of these bands relative to those of tricarbonyl-π-crotylcobalt (A_1 at 2060 cm^{-1} and E at 1994 cm^{-1}) are consistent with what is usually observed when a carbonyl group on the metal is replaced by a phosphine ligand, that is, shifts of about -75 cm^{-1} for trialkylphosphines and about -65 cm^{-1} for triphenylphosphines occur. The weak bands at 1894 and 1906 cm^{-1} undoubtedly arise from the isotopic molecules containing one ^{13}CO group. The weak bands on the high frequency sides of the strong bands for both compounds are believed to be due to an isomeric form in equilibrium with the major form since their intensities are reversibly temperature dependent.

THE BEHAVIOR OF (I) UNDER HYDROFORMYLATION CONDITIONS

The π-crotyl complex, (I), is unstable at elevated temperatures under synthesis gas* pressures in either 1-heptene, dodecane or dodecanol. It disappears with conco-

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* The term synthesis gas in used throughout to designate a mixture of hydrogen and carbon monoxide.

mitant formation of bis[tricarbonyl(tributylphosphine)cobalt] (II), tricarbonyl-π-crotylcobalt (III), the unsymmetrically substituted complex (tributylphosphine)-heptacarbonyldicobalt (IV), butenes, butane, butadiene, valeraldehydes, and amyl alcohols. The material balance of these latter C_4 and C_5 units, resulting from reaction of the π-crotyl moiety of (I) with synthesis gas, was 74-84%. Compound (II), isolated from the reaction mixtures, was identical to material described by Slaugh and Mullineaux[3]. Compound (III) was identified by comparison of the infrared spectrum with that of material previously reported[8]. Compound (IV), the tributylphosphine analog of Bor and Marko's triphenylphosphine complex[8], $Ph_3PCo(CO)_3$–$Co(CO)_4$, was identified by comparison of infrared carbonyl maxima with material prepared from the reaction of octacarbonyldicobalt with synthesis gas and one equivalent of tributylphosphine at 110–125°. Subsequent to the completion of this work, Bor and Marko and coworkers[9] independently reported the preparation and characterization of (IV).

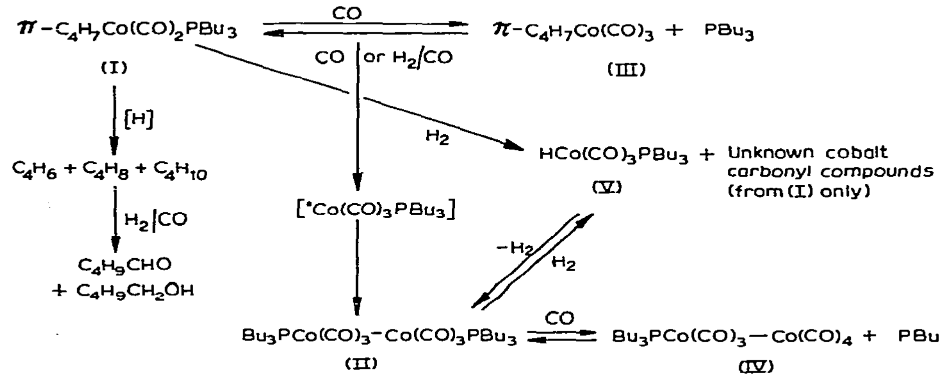
$Bu_3PCo(CO)_3$–$Co(CO)_3PBu_3$ (II) $C_4H_7Co(CO)_3$ (III) $Bu_3PCo(CO)_3$–$Co(CO)_4$ (IV)

Analogous behavior was observed when crude catalyst preparations (prior to chromatography) containing 50-65% (I) were subjected to the above conditions, with the exception that the formation of (III) and (IV) was suppressed, probably due to the presence of tributylphosphine (*vide post*).

To quantitatively investigate the fate of the various cobalt carbonyl species during this study, the reactions were monitored by infrared spectroscopy using the metal carbonyl stretching frequencies for the various complexes (Table 2). The concentrations were calculated from the infrared spectra of samples withdrawn from the reactor and allowed to reach atmospheric conditions. In addition, qualitative spectra under reaction conditions were obtained from which ratios of components could be estimated and compared with those calculated from spectra taken under atmospheric conditions.

The data plotted in Fig. 1 show the changes in concentration of the cobalt carbonyl species with time. Compound (I) rapidly disappears with concomitant formation, in the main, of (II) which maximizes to >75% of the cobalt carbonyl species present. The tricarbonyl, (III), appears in the early phases while the unsymmetrical

TRANSFORMATIONS OF (I)



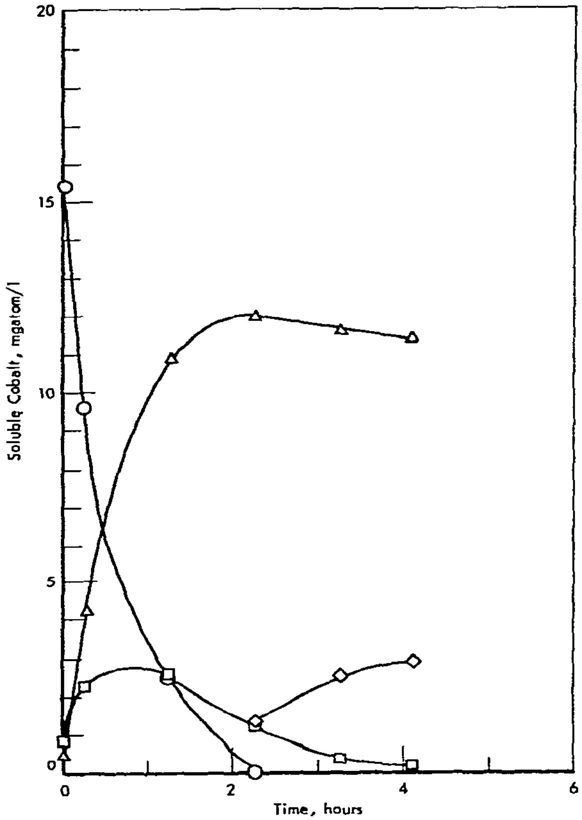


Fig. 1. Conversion of π-$C_4H_7Co(CO)_2PBu_3$ (I) under synthesis gas, 110±2°, 500 psig, $H_2/CO = 1.5$ in 1-heptene. From data of samples reduced to atmospheric conditions.
○ π-$C_4H_7Co(CO)_2PBu_3$ (I); △ $Bu_3PCo(CO)_3$–$Co(CO)_3PBu_3$ (II); □ π-$C_4H_7Co(CO)_3$ (III); ◇ $Bu_3PCo(CO)_3$–$Co(CO)_4$ (IV).

complex, (IV), appears in the latter phases of the reaction. At higher temperatures (*e.g.*, 125°, 165°, and 190°) at 500 psig of synthesis gas, the rate of disappearance of (I) is too fast to conveniently measure. In all cases, (II) is the major cobalt carbonyl species formed.

It is believed that a rapid interconversion between (I) and (III) occurs under reaction conditions. The ratio of (III) to (I) was considerably higher under reaction conditions than under atmospheric conditions. Thus, at zero time*, the ratio was 0.68 at 110° and 500 psig, compared with 0.05 at ~25° and ~15 psi, respectively, and at 0.25 h it was 1.45 and 0.27, respectively, showing that when synthesis gas was removed and the system cooled, reversion to (I) occurred. First order disappearance plots from data of samples reduced to atmospheric conditions for combined (I) and (III), *but not for (I) alone*, showed good linearity with $t_{\frac{1}{2}} = 0.6$–0.7 h. Excess tri-n-butylphosphine (total $P/Co = 1.95$) drastically suppressed the formation of (III).

Compound (IV) is formed in the latter phases of the reaction and under reaction

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* The concentrations of (II) and (III), plotted at "zero time", are the result of having heated the reaction mixture from room temperature to 110° under synthesis gas; neither was present at ambient pressures under nitrogen.

conditions is believed to arise from (II). Excess tri-n-butylphosphine not only suppressed the formation of (III) but also suppressed that of (IV). Separate experiments have shown that (IV) may be prepared by equilibrating (II) with synthesis gas at 110–125° and 600 psig.

When (I) was treated solely with carbon monoxide at 110° and 500 psig, (II) and (III) were readily formed.

Hydrogen alone at 110° and 500 psig rapidly converts (I) to several cobalt carbonyl species. Compound (II) and the hydrocarbonyl (V), $HCo(CO)_3PBu_3$, account for only about 10% of the amount of (I) converted. Major new unidentified carbonyl bands are observed at *ca.* 1954, 1790, and 1785 cm^{-1} and, possibly, at about 1988 cm^{-1}. The two low frequency bands indicate the presence of a complex which has two carbonyl groups bridging Co atoms having phosphine ligands.

These transformations are summarized in the above chart. The conversions of (I) to (III), (II) to (IV)[10] and (II) to (V) are indicated as equilibria. A coordinatively unsaturated cobalt carbonyl is postulated in the conversion of both (I) and (III) to (II). Piacenti, Bianchi, and Benedetti[10] have demonstrated that conversion of (V) to (II) readily occurs and conversely that (II) may be converted to (V) under synthesis gas.

CATALYSIS IN THE HYDROFORMYLATION OF THE 1-HEPTENE

During the period depicted in Fig. 1 in which (I) and (III) disappear, hydroformylation of the 1-heptene occurs to an extent *no greater than* 1% resulting in octanols and octanals. Compound (II) is the predominant cobalt carbonyl species formed (>75%) and, further, is always spectroscopically observed to be present when hydroformylation is first detected. When reaction mixtures were heated from ambient temperatures to 165° over 30-40 minutes (*vide post*), hydroformylation proceeded to 1.5-2.5%, compound (II) was formed to greater than 80% and compound (I) had disappeared during this interval. At the end of *ca.* five hours at this temperature, hydroformylation had proceeded to 30-40%.

Similar experiments using pure (II) as the initially added complex showed that hydroformylation proceeded in an exactly analogous manner.

Therefore, since (I) disappears rapidly at temperatures and pressures (gas) where hydroformylation rates are low and, further, completely disappears when temperatures are reached that permit reasonable hydroformylation rates, it is not possible that the π-crotyl complex (I) is the catalytic species responsible for hydroformylation.

The utility of (II) as a hydroformylation catalyst has been previously described[2,3]. Therefore, since (I) is mainly converted to (II), it is reasonable that the latter promotes hydroformylation in the present case. The conversion of (II) to (V), $HCo(CO)_3PBu_3$, and the mechanism of hydroformylation have been discussed by Slaugh and Mullineaux[2,3] and later, in response to patents of Slaugh and Mullineaux[2] by Tucci[11].

EXPERIMENTAL

Infrared spectra were measured on a Cary Model 90 double beam spectrometer operating at 3 cm^{-1} resolution over the spectral region 1500 cm^{-1} to 2100 cm^{-1}.

NMR spectra were obtained at 100 MHz using a Varian Model HR-100 instrument. Phosphorus chemical shifts were measured from an external reference, trimethyl phosphate, and proton shifts from an internal reference, hexamethyldisiloxane. Phosphorus decoupling was produced by an NMR Specialties SD-60 decoupler operating at 40.5 MHz. High resolution mass spectra were obtained with a CEC Model 21-110B spectroscope and the data processed with a Shell Development computer program[12].

Reactions involving carbon monoxide and/or hydrogen were conducted in a 300-ml Magnestir autoclave (Autoclave Engineers, Inc.) at constant pressure. Both liquid and gas samples could be withdrawn from the reactor in order to monitor the reactions. Stirring was held constant (1000 rpm) throughout the series.

Analytical procedures

Cobalt carbonyl species were determined quantitatively by infrared spectroscopy under atmospheric conditions on samples periodically withdrawn from the autoclave during reaction. Concentrations of the carbonyl species could be measured usually to within 10%. Qualitative infrared spectra were obtained under reaction conditions by use of an in-line heated pressure cell equipped with sapphire optics. This was connected to the sample valve of the autoclave by 1/8" stainless steel tubing, placed in the sample port of a Beckman Model 8 spectrophotometer, and heated to reaction temperature; samples were withdrawn at reaction pressures.

The heptenes and heptane were analyzed by GLC from samples withdrawn into cool tetradecane. The octanols, octanals, valeraldehydes and amyl alcohols were analyzed by GLC using a column consisting of neopentylglycol sebacate deposited on Chromosorb W. In addition, samples were withdrawn into sodium borohydride and the total alcohol content determined on the same GLC column for comparison purposes.

The valeraldehydes resulting from the hydroformylation of the butenyl moiety of (I) were unequivocally identified by high resolution mass spectrometry.

The butenes, resulting from hydrogenolysis of the butenyl portion of (I), were unequivocally identified by separation on an SF 96 capillary GLC column, the effluents from which were monitored with a quadrupole mass spectrometer* (EAI, Quad 300; Electronic Associates, Inc.). Routine quantitative analyses of butenes and butane were performed by GLC on a dimethylsulfolane column.

Dicarbonyl(tributylphosphine)-π-crotylcobalt (I)

This was prepared according to Mertzweiller and Tenney[1] by allowing tetracarbonylhydridocobalt [prepared *in situ* from cobalt(II) 2-ethylhexanoate (Witco Chemical Company) and synthesis gas in hexane] to react with butadiene followed by reaction with freshly distilled tri-n-butylphosphine. The intermediate, tricarbonyl-π-crotylcobalt, was not isolated in this sequence (*vide post*). The crude hexane solutions were extracted with saturated sodium bicarbonate solutions, back-extracted with water to pH 6–7, dried ($MgSO_4$) and concentrated under reduced pressure. The crude complex (II) was further purified by chromatography on Florisil (Floridin Company) by elution with hexane in a nitrogen atmosphere. The air-sensitive reddish-orange

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* We are indebted to C. E. Muller and A. K. Irikura for these analyses.

oil was stored under CO. (Found: C, 58.0; H, 9.6; Co, 14.6; O, 8.4; P, 8.6; mol. wt. ebullioscopic in benzene, 390±20. $C_{18}H_{34}CoO_2P$ calcd.: C, 58.04; H, 9.20; Co, 15.83; O, 8.59; P, 8.32%; mol. wt., 372.)

The NMR spectra of "aged" samples, even though they were kept in inert atmospheres, showed considerable line broadening, indicating the presence of paramagnetic material.

By infrared comparison of crude sample preparations with those of analytical samples, compound (I) was estimated to be present in these preparations to the extent of 50-65%. Additional colored bands on the chromatographic columns could not be eluted, even with solvents more polar than hexane; their identities are unknown. Free tributylphosphine was found by GLC to be present in the crude reaction products.

Bis[tricarbonyl(tributylphosphine)cobalt] (II)

This was prepared according to Slaugh and Mullineaux[2,3] and also according to Piacenti and coworkers[10]. No differences existed in the final crystallized samples, m.p. 134-135° (evacuated tube). The infrared spectra in hexane were the same prior to evacuation as they were after evacuation and prior to melting.

Tricarbonyl-π-crotylcobalt (III)

This was prepared according to McClellan *et al.*[6]. The dark-red, air-sensitive liquid was purified by bulb-to-bulb distillation at 0.05 mm pressure.

The treatment of dicarbonyl(tributylphosphine)-π-crotylcobalt (I) under hydroformylation conditions

The following is illustrative of several experiments conducted during this investigation. The autoclave was charged under nitrogen with freshly purified (I) (0.700 g, 99.5% pure), freshly distilled 1-heptene (88.2 g, 0.84 mole) and n-nonane (0.808 g) as an internal GLC marker. Initial infrared analysis (under nitrogen and prior to pressuring the system with synthesis gas) showed the concentration of (I) to be 0.0153 *M*; neither (II), (III), (IV), nor (V) was detected. The system was rapidly heated to 110° at 530–550 psig of synthesis gas ($H_2/CO = 1.5$) over 16 min. At this point the concentration of (I) had decreased to 0.0128 *M*: bis[tricarbonyl(tributylphosphine)cobalt] (II), 0.0009 *M*; the tricarbonyl (III), 0.0006 *M*; and aldehyde (maximum at 1735 cm^{-1}), 0.003 *M* were detected. At the end of 5 h, the complex (I) had completely disappeared and the complex (II) represented 86% of the total cobalt carbonyl species present. The complex (IV) accounted for the remainder (14%) of the carbonyl species. Infrared analysis for aldehyde at the end of this time period showed that it had been formed to 0.10–0.15% based on starting olefin. Analysis for C_8 alcohols and aldehydes indicated the same order of conversion. The C_8 aldehyde to C_8 alcohol ratio was $\geqslant 4/1$. Olefin analyses from a composite of several reactions showed that no more than 1% of the heptenes were hydroformylated during this period to 5 h.

A reaction in which purified (I) was initially present at 0.068 *M* in 1-heptene was conducted and monitored in the same manner. The reaction profile of the cobalt carbonyl species was quite similar to that depicted in Fig. 1. The material balance of products resulting from the butenyl moiety of (I) was 84%. The ratio of C_4 hydrocarbons to C_5 hydroformylation products was 52/48. The normalized distribution of C_4 hydrocarbons was: butane, 18.1; 1-butene, 23.3; *trans*-2-butene, 30.4; *cis*-2-butene, 28.2%; small amounts of butadiene and methane were detected. The major hydroformylation product from the butenyl entity of (I) was n-valeraldehyde; small amounts of branched valeraldehydes, n-amyl alcohol and branched amyl alcohols were formed.

Isolation of bis[tricarbonyl(tributylphosphine)cobalt] (II) after treatment of (I) under hydroformylation conditions

This entire operation was conducted under carbon monoxide. A reaction mixture in which (I), initially present at 0.068 *M* in dodecane, had been treated for 24 h at 110° with synthesis gas at 500 psig, was cooled to room temperature. The infrared spectrum showed the major cobalt carbonyl component to be (II) (*ca.* 75%); (I) was not observed. The reaction mixture was cooled, the dark red crystals collected and crystallized thrice from hexane by alternate cooling (−78°) and centrifugation (0°). The crystals were dried for 24 h at 0.1 mm, m.p. 134–135° (evac. tube). (Found: C, 51.9; H, 7.7; Co, 18.2; P, 9.6. $C_{30}H_{54}CoO_6P_2$ calcd.: C, 52.21; H, 7.88; Co, 17.07; P, 8.97 %.)

The infrared spectrum and the X-ray powder diagram were indistinguishable from those of authentic material[2,3].

Dicarbonyl(triphenylphosphine)-π-crotylcobalt

This was prepared by a modification of the method of Heck and Breslow[4]. A solution of octacarbonyldicobalt (17.06 g, 0.05 mole) in hexane (125 g) was heated for 1 h at 146° under 1200–1260 psig of synthesis gas ($H_2/CO=2$). The temperature was lowered to 106° and a solution of butadiene (10.5 g, 0.19 mole) in hexane (25 g) added from a pressure-compensated stainless steel injection vessel attached to the reactor. The mixture was stirred for 2.1 h at 99–101° under 1200 psig of synthesis gas. The autoclave was cooled to room temperature, depressurized to 200 psig and slowly forced into a stirred solution of triphenylphosphine (26.2 g, 0.1 mole) in ether (50 g) maintained at atmospheric pressure. After the evolution of carbon monoxide had ceased, the solvent was removed under reduced pressure to leave 43.0 g of red-brown solid.

The product was extracted with several portions of ether under nitrogen and the ether evaporated to leave 25.2 g of semi-solids. A portion (2.9 g) was chromatographed on 90 g of alumina (Woelm grade 1) by elution with ether (250 ml); a bright orange solid was recovered and crystallized thrice from ether/hexane under carbon monoxide, m.p. 93.2–95.5° (dec.), reported[4] 91.5–94° (dec.).

(Tributylphosphine)heptacarbonyldicobalt (IV)

A solution of octacarbonyldicobalt (1.71 g, 0.005 mole) and freshly distilled tri-n-butylphosphine (1.11 g, 0.055 mole) in n-pentane was heated at 125° under 600 psig of synthesis gas ($H_2/CO=2$) for 20 h. Infrared analysis, taken under atmospheric conditions, showed the presence of both (II) and (IV).

A 5 ml aliquot was chromatographed on Florisil by elution with n-hexane in a carbon monoxide atmosphere. From the second, third and fourth 250-ml fractions was obtained 0.13 g of red-brown solid. No evidence for (II) was found in these fractions and apparently was eluted at a much slower rate than was (IV).

The solid was crystallized from n-hexane under CO at −78° by centrifugation, m.p. (evacuated) 62.5–65° (dec.). (Found: C, 44.1; H, 5.2; Co, 21.1; P, 5.8. $C_{19}H_{27}Co_2O_7P$ calcd.: C, 44.20; H, 5.27; Co, 22.83; P, 6.00 %.) Most of the stronger carbonyl bands for recrystallized (IV) in hexane compare well with those reported by Bor and Marko[8] for the triphenylphosphine and, more recently, for the tributylphosphine[9] analog.

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