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NOVEL HYDROFORMYLATION* CATALYSTS

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SUMMARY

Cobalt carbonyl complexes containing a complementary tertiary phosphine, arsine or phosphite ligand, e.g., $[Co(CO)_3PBu_3]_2$, have catalytic properties for the hydroformylation of olefins which are considerably different from those of dicobalt octacarbonyl. These novel catalysts are unusual because many are active at low pressures (100–300 psi), produce alcohols rather than aldehydes as the primary product and exhibit a high preference for reaction at the terminal carbon position of 1-olefins.

INTRODUCTION

The "OXO" or hydroformylation reaction, in which aldehydes are produced as principal products from olefins, carbon monoxide and hydrogen, is technically very important. Dicobalt octacarbonyl, either introduced directly or formed *in situ*, is the conventional catalyst (*vide infra*) that has been used for the reaction. We have shown[1] that complexes of cobalt with carbon monoxide and a complementary phosphine, arsine or phosphite ligand have catalytic properties for the hydroformylation reaction which are considerably different from those of the conventional cobalt carbonyl catalyst**. At this time, we would like to report on some of the interesting observations that have been made.

RESULTS AND DISCUSSION

The hydroformylation catalysts generally were formed *in situ* by treating $Co_2(CO)_8$ with the complementary ligand (ligand/cobalt mole ratio = 1/1 to 2/1), carbon monoxide and hydrogen (H_2/CO mole ratio = ~2/1) at 300–800 psi and 150–200°. The olefin substrate was added either with the catalyst precursors or after preforming the catalyst. Cobalt salts, *e.g.* cobaltous acetate, can be used instead of $Co_2(CO)_8$. In these cases, the cobalt salt is rapidly reduced to give the same cobalt

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* The term hydroformylation is used here to denote the addition of carbon monoxide and hydrogen to a carbon–carbon double bond to form either aldehydes or alcohols.

** Heck and Breslow[2–4], while studying the mechanism of the hydroformylation reaction, have identified metal complex intermediates of the reaction by treating alkyl- and acyl-cobalt carbonyls with triphenylphosphine. However, they did not determine the effect of the complementary ligand on the hydroformylation reaction *per se*.

complex as obtained above. All of the catalyst solutions had a characteristic deep red color. Although most of the examples given below employ 1-pentene as the olefin substrate, similar results have been obtained for other terminal olefins, such as propylene and 1-butene.

When $Co_2(CO)_8$ is treated with Bu_3P at elevated temperatures (*e.g.* 150°) under CO and H_2 pressure, two compounds, one red and one yellow, are formed which have been identified as $[Co(CO)_3PBu_3]_2$ (I) and $[Co(CO)_3(PBu_3)_2]^+[Co(CO)_4]^-$ (II), respectively. (I) is the principal complex isolated from the recovered hydroformylation products. As shown by X-ray techniques, (I) in crystalline form possesses a metal–metal bond without the benefit of bridging carbonyl groups. The details of the structure determination is to be reported separately by Professor J. A. Ibers. Under hydroformylation conditions, (II) is converted to (I) which is easily isolated from the product mixture. Also, (I) is probably converted partially to, and in equilibrium with, the hydride $HCo(CO)_3PBu_3$ (III) (*vide infra*). For convenience of discussion, we will label this catalyst system (I) even though other tri-n-butylphosphine-containing cobalt carbonyl complexes may be present during hydroformylation.

TABLE 1

HYDROFORMYLATION OF 1-PENTENE WITH COBALT CARBONYL CATALYSTS CONTAINING A COMPLEMENTARY LIGAND[a]

Solvent, n-hexane or n-octane, 20 ml; 1-pentene, 65 mmoles; catalyst, 2 mmoles (based on Co in monomeric form); reaction times at 195° were ~3 h; maximum total pressure, 450–500 psi; complementary ligand/cobalt mole ratio was 1 for expts. 12 and 13 and 2 for all others; H_2/CO mole ratio was ~2; conversion of 1-pentene was generally 75–100% except for expt. 10 which was 40%.

Expt. No.	Complementary ligand	Temp. (°C)	Rate of gas reaction[b]	Conv. of 1-pentene (%)	Total yield[c]		Prod. compn.[d]	
					Alcohols	Aldehydes	Normal	Branched
1	Et_3P	195	220	100	79.8	0	80.9	19.1
2	Bu_3P	195	265	100	77.0	0	84.1	15.9
3	Bu_3P	150	29	98.1	83.7	1.4	91	9
4	$(Cyclo\text{-}C_6H_{11})_3P$	195	200	75.4	69.6	3.0	79.5	20.5
5	$(2\text{-}Et\text{-}C_6H_{12})_3P$	195	154	72.0	65.9	3.9	67.2	32.8
6	$PhEt_2P$	195	206	100	75.6	2.8	79.0	21.0
7	Ph_2EtP	195	314	100	74.5	4.3	74.5	25.5
8	$PhBu_2P$	195	>265	100	72.0	0	80.0	20.0
9	$PhBu_2P$	150	57	79.4	76.4	12.3	88.4	11.6
10	Ph_3P	195	19.8	39.9	60.7	10.3	66.0	34.0
11	$Ph_2PCH_2CH_2PPh_2$	195	57	96.2	67.7	1.3	56.5	43.5
12	$Ph_2P(CH_2)_4PPh_2$	195	140	100	82.2	0	74.7	25.3
13	$Ph_2P(CH_2)_5PPh_2$	195	230	100	80.1	4.5	73.9	26.1
14	Bu_3As	150	206	82.8	51.9	28.7	67.8	32.2
15	$PhEt_2As$	150	290	98.9	66.6	18.4	55.7	44.3

[a] Catalysts were prepared *in situ* by adding the complementary ligand to $Co_2(CO)_8$. [b] Initial rate of gas consumption, in mmoles/h, was measured before 5% of the 1-pentene had reacted. [c] Based on converted 1-pentene; 100% − combined yields of alcohols and aldehydes = yield of n-pentane. For convenience in making comparisons, the yields were normalized to 100%. However, the material balances for the GLC analyses were usually ~97–100%, indicating that little higher molecular weight material was formed. [d] Normal refers to n-hexanol and n-hexanal combined. Branched products consist mainly of 2-methylpentanol and a little 2-methylpentanal.

Rather drastic conditions are used for hydroformylation with $Co_2(CO)_8$. To prevent catalyst decomposition at 100–180°, combined pressures of ~1500 to 4500 psi of hydrogen and carbon monoxide are customary[5]. On the other hand, cobalt complexes containing carbon monoxide and a complementary ligand of a type described above can be used at low pressures. For example, (I) is an active catalyst at ~150–200° under combined hydrogen/carbon monoxide (2:1 mole ratio) pressures as low as 100–300 psi. In general, the trialkylarsine/carbonyl cobalt catalysts are somewhat less stable than the corresponding tertiary phosphine-containing complexes. With the former, it is preferable to employ a somewhat lower temperature ($\leqslant$ 150°) than that usually used for the latter ($\geqslant$150–200°).

The hydrogenation activity of $Co_2(CO)_8$ is not high, consequently, aldehydes are the primary products[5]. Interestingly, the hydrogenation acitivity of (I) is greater and alcohols can be obtained in high yields in a single operation. For example, under identical conditions (150°; 500 psi; H_2/CO mole ratio 1.0) with 50% of 1-pentene converted in each case, (I) and $Co_2(CO)_8$ produced hexyl aldehydes and hexyl alcohols in the ratios of 30/70 and 95/5, respectively. During these comparative experiments with limited 1-pentene substrate, part of the $Co_2(CO)_8$ catalyst decomposed to cobalt metal. As shown in Table 1, several catalysts similar to (I) which were prepared *in situ* also produced principally alcohols rather than aldehydes.

The ratio of aldehydes to alcohols in the hydroformylation products is dependent on the reaction temperature. At 195° with H_2/CO mole ratio equal to 1.0 and the Bu_3P/cobalt mole ratio equal to 2.0*, the hydroformylation product, with 20% of the 1-pentene substrate reacted, consisted of 85% hexyl alcohols and 15% hexyl aldehydes. At 150° with the same catalyst system and the same conversion of 1-pentene, the product consisted of 15% hexyl alcohols and 85% hexyl aldehydes. In the latter case, the aldehyde concentration rapidly decreased so that by the time 50% of the 1-pentene had reacted, the product consisted of 70% hexyl alcohols and 30% hexyl aldehydes. It is evident from the temperature effect that the heat of activation for the hydrogenation of the intermediate aldehydes to alcohols in the presence of (I) is larger than that for the hydroformylation of the olefin substrate to the corresponding aldehydes.

Hydroformylation with $Co_2(CO)_8$ as catalyst frequently is accompanied by aldehyde condensation reactions so that considerable higher boiling material is formed. With (I) and similar catalysts, the by-product is quite low, presumably because the concentration of the aldehydes is relatively low during the experiment.

As would be expected in view of the hydrogenation activity of (I), part of the olefin substrate is hydrogenated to the saturated hydrocarbon under hydroformylation conditions. The degree of olefin hydrogenation is markedly increased by branching, especially if the branching is on the double bond of the 1-olefins. For example, at 195° with $H_2/CO = 2.0$ and n-Bu_3P/cobalt = 2.0, 23% and 43% of 1-pentene and isobutylene, respectively, were hydrogenated concomitantly during hydroformylation. The extent of olefin hydrogenation diminishes as the reaction temperature is lowered.

It is well known that hydroformylation of olefins with $Co_2(CO)_8$ produces a mixture of isomeric aldehydes. The published data are not in complete agreement

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* (I) was prepared *in situ* under hydroformylation conditions by adding Bu_3P to $Co_2(CO)_8$.

as to the composition of these products. According to Keulemans, Kwantes and Van Bavel[6] the isomer distribution of alcohols derived from 1-pentene is 50–55% 1-hexanol, 35–40% 2-methyl-1-pentanol and 10% 2-ethyl-1-butanol. Goldfarb and Orchin[7] reported 80% 1-hexanol and 14–18% 2-methyl-1-pentanol from 1-pentene ($H_2/CO = 1.0$; 110°; 1625 psi). In both cases, the intermediate aldehydes were subsequently hydrogenated to alcohols before determining the isomer distribution of the product. Discrimination due to different rates of condensation of the isomeric aldehydes during the hydroformylation and hydrogenation operations could be partially responsible for the variations observed in the isolated products. Condensation reactions may be particularly significant in the case[7] where basic Raney nickel was used to catalyze the hydrogenation of the aldehydes to alcohols.

Even though $Co_2(CO)_8$ tends to decompose to cobalt metal at low pressures, we attempted to determine the isomeric composition of the product obtained with this catalyst under the same conditions (~400 psi) as those used for (I) (Table 2).

TABLE 2

HYDROFORMYLATION OF 1-PENTENE WITH $Co_2(CO)_8$ AS CATALYST

Solvent, n-hexane or n-octane, 20 ml; 1-pentene, 65 mmoles; $Co_2(CO)_8$, 1 mmole; reaction times, ≤ 1.0 h.

Expt. No.	Temp. (°C)	Max. press. (psi)	H_2/CO ratio	Rate of gas reaction[a]	Total yield[b]		Product compn.		Conv. of 1-pentene (%)
					Alcoh.	Aldeh.	Normal	Branched	
16[c]	100	400	1.0	~53	2.8	96.7	50	50	67
17	120	1700	1.9	~1890	3.3	95.6	70	30	97.3
18	140	1700	1.9	~3180	9.7	84	64	36	100
19[c]	150	400	1.0	≥300	4.5	90.5	50	50	47

[a] Initial rate of gas consumption, in mmoles/h, was measured before 5% of the 1-pentene had reacted. [b] Based on converted 1-pentene; 100% − combined yields of alcohols and aldehydes = yield of n-pentane. For convenience in making comparisons, the yields were normalized to 100%: the material balances for the GLC analyses ranged from 78% to ~98%, indicating that higher molecular weight material was formed. [c] Catalyst underwent decomposition to cobalt metal.

The product formed before the catalyst decomposed consisted approximately of a 1/1 mixture of normal and branched aldehydes (expts. 16 and 19). At a higher pressure (~1700 psi) and a higher H_2/CO mole ratio (2/1), the content of normal products was greater, *i.e.*, 64–70% (expts. 17 and 18).

With (I) as the catalyst, an unusually high preference for reaction at the terminal carbon position of 1-olefins has been observed. For example, the n-hexanol content of the hexyl alcohol product obtained from 1-pentene at 150° (500 psi; $H_2/CO = 2$) was 91% (expt. 3). A similar result was obtained with propene. The isomer distribution of the product is dependent upon the reaction temperature. At 195° n-hexanol was 84% of the hexyl alcohol. An analogous temperature effect also was noted with a modified cobalt carbonyl catalyst where the complementary ligand was di-n-butylphenylphosphine (expts. 8 and 9).

One step of the mechanism of hydroformylation with the conventional catalyst involves the addition of $HCo(CO)_4$, formed *in situ* from $Co_2(CO)_8$, to the olefin double bond[8]. The isomeric composition of the final product is determined by the direction of this addition. The studies of Heck and Breslow indicate that at

0° the addition of $HCo(CO)_4$ to 1-pentene gives a 50:50 mixture of $CH_3(CH_2)_4$-$Co(CO)_4$ and $CH_3(CH_2)_2CH(CH_3)Co(CO)_4$ plus $CH_3CH_2CH(CH_2CH_3)Co$-$(CO)_4$*. These results are consistent with those of Keulemans, Kwantes and van Bavel[6] and those of ours obtained at low pressures with $Co_2(CO)_8$ where the isomer distribution of the product from 1-pentene was ~50–55% of the normal and 50–45% of the branched hexyl aldehydes and alcohols. It seems likely that hydroformylation with (I) and similar catalysts proceeds via the same mechanism as that for $Co_2(CO)_8$. Consequently, the product isomer composition would reflect the direction of addition of $HCo(CO)_3PBu_3$ to the double bond. This is particularly true in this case because condensation reactions which might alter the initial product composition are very small. The results indicate that $HCo(CO)_3PBu_3$ adds to 1-pentene to give predominantly $CH_3CH_2CH_2CH_2CH_2Co(CO)_3PBu_3$ (91% at 150°). Whereas $HCo(CO)_4$ adds essentially as a neutral reagent to 1-pentene, $HCo(CO)_3PBu_3$ behaves more as a hydridic reagent. This is in keeping with the relative acidities of the two reagents. That is, replacing one of the CO groups of $HCo(CO)_4$ by a tertiary phosphine greatly reduces the acidity of the metal hydride. (When the phosphine is Ph_3P the acidity is reduced by ~7 PKa units[9].) With isobutene as the olefin substrate, the $Co(CO)_3PBu_3$ moiety adds even more exclusively to the terminal position, *i.e.* $\geqslant$96% at 195°. This trend towards more terminal addition of the metal-containing moiety in going from 1-pentene to isobutene also has been observed for $HCo(CO)_4$ at elevated temperatures (120°)[10]. Interestingly, the direction of addition of $HCo(CO)_4$ to isobutylene at 0° is essentially the reverse of that observed at elevated temperatures[8]. The direction of addition of $HCo(CO)_4$ to 1-pentene does not appear to be greatly affected by temperature changes[8]. With $HCo(CO)_3PBu_3$, apparent terminal addition to 1-pentene increases as the reaction temperature is lowered: terminal addition is 84% at 195° and 91% at 150°.

As shown by the data in Table 1, the isomeric composition of the product may vary with the complementary ligand. For catalysts containing Bu_3P (expt. 2), $PhEt_2P$ (expt. 6) or Ph_3P (expt. 10), the n-hexanol content of the hexyl alcohol product obtained from 1-pentene at 195° was 84.1%, 79.0% and 66.0%, respectively. Arsine-containing catalysts appear to be less selective for terminal hydroformylation of 1-pentene than are the corresponding tertiary phosphine-containing catalysts. For example, the normal isomer contents of the products obtained at 150° were 91.0% with Bu_3P (expt. 3), 67.8% with Bu_3As (expt. 14), ~86% with $PhEt_2P$ (estimated from data obtained at 195°, expt. 6), and ~56% with $PhEt_2As$ (expt. 15) as the complementary ligands.

Measurement of reaction rates under hydroformylation conditions by following the fate of substrates in the liquid phase is rather difficult. However, rough comparisons of catalysts have been made simply by measuring the rate of gas consumption from the pressure decline in a closed autoclave system. This technique would be most accurate for very similar catalysts where the profile of product formation is nearly the same; *e.g.* for $[Co(CO)_3PR_3]_2$ catalysts where only R is varied. In comparing $Co_2(CO)_8$ with the modified catalysts, only gross comparisons are justified because the amount of H_2 consumed varies depending on the relative amounts of aldehydes, alcohols and saturated hydrocarbons formed. To minimize effects due to changing

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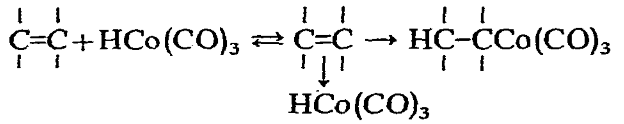
* Heck and Breslow believe that roughly the same ratio obtains at 120° also.

gas composition during the course of the experiment, the rate of gas consumption (mmoles/h) was measured early in the experiment before ~5% of the olefin had reacted.

The data in Table 1 show that the rate of hydroformylation is influenced by the complementary ligand. The observed rates ranged by a factor of ~15 for catalysts containing various complementary tertiary phosphine ligands (compare expts. 7 and 10). It appears that catalysts containing tertiary arsines are more active than the corresponding catalysts containing tertiary phosphines. At 150° the rates are at least 7 times greater with a Bu_3As-containing catalyst than they are with (I) (expts. 3 and 14). The rate data collected for $Co_2(CO)_8$ are minimum values since catalyst decomposition and deactivation at low pressures was taking place during the course of the experiment. A comparison of expts. 19 (Table 2), 3 and 14 (Table 1) indicates that $Co_2(CO)_8$ is more active than either the Bu_3As-containing catalyst or (I). Limited rate data obtained with catalysts containing tertiary phosphites, such as $(EtO)_3P$, indicate that they are not as active as (I). Typically, rates at 195° were ten times greater with the latter.

Heck and Breslow[8] have concluded from their mechanism studies that $Co_2(CO)_8$ is cleaved by hydrogen under hydroformylation conditions to form $HCo(CO)_4$. The latter then either adds to the olefin double bond or, more likely, loses a CO to form $HCo(CO)_3$ which coordinates with the olefin before insertion into the hydrogen–cobalt bond occurs (eqns. 1 and 2). Subsequent insertion of CO into the newly formed carbon–cobalt bond followed by hydrogen cleavage of the resultant acylcobalt intermediate produces the aldehyde product. It seems likely that the mechanism of reaction with (I) and analogous complexes is similar to that for $Co_2(CO)_8$. In response to our patents issued on the modified catalyst systems[1], Piacenti, Bianchi and Benedetti[11] have investigated (I) and shown that it is indeed cleaved by H_2 to form $HCo(CO)_3$-PBu_3 and that the latter adds to olefins but at a considerably lower rate than does $HCo(CO)_4$. The slower rate of addition of $HCo(CO)_3PBu_3$ may explain why (I) and similar catalysts are less active than $Co_2(CO)_8$. The addition reaction *per se* may be rate limiting or possibly the presence of the phosphorus-containing ligands decreases the rate at which the olefin replaces one of the CO groups prior to the insertion (addition) of the olefin into the hydrogen–cobalt bond. Ligand exchange studies for several different metal carbonyl systems have shown that replacement of one CO group generally decreases the rate of exchange for the remaining CO groups[12,13].

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (1)$$



$$\begin{array}{c}|\;\;|\\ C{=}C\\ |\;\;|\end{array} + HCo(CO)_3 \rightleftharpoons \begin{array}{c}|\;\;|\\ C{=}C\\ |\downarrow|\\ HCo(CO)_3\end{array} \rightarrow \begin{array}{c}|\;\;\;|\\ HC{-}CCo(CO)_3\\ |\;\;\;|\end{array} \qquad (2)$$

Osborn, Wilkinson and Young reported that a rhodium complex, 1,2,3-tris-(triphenylphosphine)trichlororhodium(III), catalyzes the hydroformylation of olefins[14]. For example, at 55° and ~1300 psi total pressure ($H_2/CO=1.0$), 1-hexene was converted to n-heptanal (~70%) and 2-methylpentanal (~20%). Under the same conditions employed for the above modified cobalt catalysts, we had prepared a rhodium catalyst[4] *in situ* by adding tri-n-butylphosphine to $RhCl_3$ (Bu_3P/Rh mole ratio$=2.0$). Sodium acetate was included to remove any HCl liberated as the catalyst formed under hydroformylation conditions. In the absence of the added Bu_3P, a stable catalyst was not obtained whereas with the complementary ligand present a catalyst active at low pressures resulted. Compared to (I), the rhodium catalyst at 195° and 500 psi of hydrogen and carbon monoxide (2 : 1 ratio) is more selective for the formation of aldehydes. With ~37% of 1-pentene reacted, a 4/72 and 92/1 aldehyde/alcohol product mole ratio was obtained with (I) and the rhodium catalyst, respectively. Even with 85% of the 1-pentene converted, the aldehyde/alcohol product ratio was 60/25 for the latter catalyst. High aldehyde yields have also been observed for tertiary phosphite-containing rhodium catalysts[15].

This particular rhodium catalyst is not as selective as (I) for hydroformylation at the terminal position of 1-pentene. At 195°, the normal/branched isomer ratios of the hydroformylation products were 60/40 and 84/16, respectively.

EXPERIMENTAL

Hydroformylation procedures

The following procedure illustrated with the complementary ligand tri-n-butylphosphine is typical for all the experiments discussed in the text and listed in the tables.

n-Octane (20 ml), sublimed dicobalt octacarbonyl (0.34 g, 1.0 mmole), 1-pentene (64 mmoles) and tri-n-butylphosphine (4.0 mmoles) were placed in an 85-ml stainless steel autoclave. After the vessel was sealed, a mixture of hydrogen and carbon monoxide (~2.1/1 mole ratio) was introduced. The system was then heated to the desired reaction temperature (150–200°) by placing the vessel in a brass cup which was wrapped with a heating coil. Stirring was provided by a Teflon covered bar magnet placed inside the autoclave. The magnet was rotated by an external magnetic stirrer. The pressure decrease resulting from consumption of hydrogen and carbon monoxide was recorded on a suitable recorder. The gases were frequently replenished so that the pressure was maintained within a narrow range, usually 400–500 psi. The time required to complete the experiment varied with the catalyst from 1.0 h to 3 or 4 h.

The dicobalt octacarbonyl used for catalyst preparation can easily be replaced with cobalt salts, such as cobaltous acetate. The experimental procedure remains the same. The catalysts also can be prepared separately and then mixed with the other reagents in the autoclave.

Product analysis

The hydroformylation products in each instance were determined by gas chromatographic (GLC) analyses of the recovered solutions. Individual components of the products were trapped as they emerged from the chromatography unit and were identified by mass spectrometric and infrared analyses. A 25-ft. column packed with Craig polyester-succinate on 40–60 mesh firebrick (Varian Aerograph) was found suitable for analysis of aldehydes and alcohols. A column packed with DC-710 (silicone oil) on firebrick was suitable for analysis of the hydrocarbon products. When catalysts containing complementary ligands were used, the material balances for the GLC analyses were usually excellent (~97–100%) indicating that little higher molecular weight material was formed. When dicobalt octacarbonyl was employed, the material balances for the analyses were as low as 78%.

Isolation of $[Co(CO)_3PBu_3]_2$ *(I) and* $[Co(CO)_3(PBu_3)_2]^+[Co(CO)_4]^-$ *(II)*

In a 210-ml, magnetically stirred autoclave (same type as described above) were placed dicobalt octacarbonyl (13.6 g; 0.04 mole), tri-n-butylphosphine (40 ml; 0.16 mole) and isopentane (100 ml). Hydrogen and carbon monoxide (2/1 mole ratio) were introduced and the autoclave heated to 150° (600 psi) for 1 h. A greenish-yellow solid was collected by filtration of the recovered product solution. Upon recrystallization from ethanol (temperature not allowed to exceed 50°), 2.38 g (8.3% yield) of a yellow crystalline solid was obtained. The original red colored isopentane filtrate was evaporated by passing N_2 through the solution. The red crystals thus obtained were recrystallized several times from isooctane or n-hexane. The crystals were a red color: yield, 12.1 g of 43.8% of theoretical. All of the above operations were performed in a N_2-filled dry box to avoid air oxidation. With similar technique, mainly (I) was isolated from hydroformylation products.

The yellow compound is believed to be $[Co(CO)_3(n\text{-}Bu_3P)_2]^+[Co(CO)_4]^-$ (II) which also was reported by Piacenti, Bianchi and Benedetti[11]. The infrared data are consistent with that reported[11]; however, the melting point we obtained is higher, *i.e.* 120–121° compared to 109–110° (with decomp.) obtained by the Italian workers. The ionic character of the yellow complex is consistent with its solubility characteristics. It is soluble in the polar solvents dimethyl formamide, benzonitrile, acetonitrile, methyl benzoate, acetone and acetophenone. To a lesser extent it is soluble in diphenyl ether, ethanol and acetic acid. The material is quite insoluble in benzene or other hydrocarbon solvents, thus, making cryoscopic molecular weight determinations difficult. A measured cryoscopic molecular weight of the yellow crystals in acetophenone was ~510 (calcd. 718). X-ray data by Prof. J. A. Ibers gave a value of 345 ± 10 for the unit molecular weight or 694 ± 21 for a dimeric cobalt unit. (Found: C, 51.9; H, 7.7; Co, 16.4; P, 8.6. $C_{31}H_{54}Co_2O_7P_2$ calcd.: C, 51.8; H, 7.6; Co, 16.4; P, 8.6%.)

The composition of the red compound (I) has been shown unequivocally by a detailed X-ray structure determination (work to be reported separately by Prof. J. A. Ibers) to be $[Co(CO)_3PBu_3]_2$. The material is non-ionic and has no carbonyl groups bridging the two metal atoms which are bonded together. The m.p. of the material varies with the technique of handling. In an open tube, the m.p. ranges from ~118–124; however, in an evacuated sealed tube, a m.p. of 134–135° was observed (appreciation is expressed to Dr. W. W. Spooncer for obtaining the m.p. data). Detailed infrared data on (I) is to be reported separately by Dr. A. C. Jones. (Found: C, 52.3; H, 7.9; Co, 17.0; P, 8.7. $C_{30}H_{54}Co_2O_6P_2$ calcd.: C, 52.2; H, 7.9; Co, 17.1; P, 9.0%.)

Under hydroformylation conditions (II) is converted to (I). Refluxing an isooctane solution of (II) also produced (I)[11].

(I) and (II) are analogous to a variety of other complexes reported in the literature[16–18] which also have been prepared by the reaction of the extraneous ligand with $Co_2(CO)_8$.

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