Journal of Organometallic Chemistry, 236 (1982) 381—384
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTION OF TRIPHENYLCARBINOL WITH $HCo(CO)_4$

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(Received March 22nd, 1982; in revised form May 27th, 1982)

Summary

The reaction of Ph_3COH with 2 mol of $HCo(CO)_4$ gives Ph_3CH in quantitative yield. The reaction is cleanly second order ($k_2 = 2.50 \times 10^{-4}$ l mol^{-1} s^{-1}, in CH_2Cl_2 at 20°C), first order with respect to each reactant. The rate increases markedly with increase in solvent polarity, suggesting Ph_3C^+ as an intermediate. The rate of the reaction of $HCo(CO)_4$ with $Ph_3\overset{+}{C}\overset{-}{B}F_4$ is more than 10^3 as fast as with Ph_3COH. No evidence for the functioning of $HCo(CO)_4$ as a hydride donor could be secured.

Introduction

The room temperature stoichiometric reaction between Ph_3COH and $HCo(CO)_4$ to give Ph_3CH was first reported almost thirty years ago [1]. After it became clear that aromatic carbinols probably react with $HCo(CO)_4$ via intermediate carbocations [2], it was suggested [3] without experimental evidence, that the reaction pathway with Ph_3COH was made possible by the strong acid character of $HCo(CO)_4$ and consisted of the following steps:

$$Ph_3COH + HCo(CO)_4 \rightleftharpoons Ph_3C\overset{+}{O}H_2 + Co(CO)_4^- \qquad (1a)$$

$$Ph_3C\overset{+}{O}H_2 \rightleftharpoons Ph_3\overset{+}{C} + H_2O \qquad (1b)$$

$$Ph_3\overset{+}{C}\,\overset{-}{Co}(CO)_4 \rightleftharpoons Ph_3C\cdot + \cdot Co(CO)_4 \qquad (1c)$$

$$Ph_3C\cdot + HCo(CO)_4 \rightarrow Ph_3CH + \cdot Co(CO)_4 \qquad (1d)$$

$$2\,\cdot Co(CO)_4 \rightarrow Co_2(CO)_8 \qquad (1e)$$

$$Ph_3COH + 2HCo(CO)_4 \rightarrow Ph_3CH + H_2O + Co_2(CO)_8 \qquad (1)$$

However, it is possible that reaction 1b could be followed by direct hydride abstraction from $HCo(CO)_4$. It has recently been shown [4] that $HMn(CO)_5$ can function as a hydride donor in the presence of a strong acid. There is no such evidence for $HCo(CO)_4$ functioning in the same capacity although it is

0022-328X/82/0000—0000/$02.75

conceivable that carbocations might induce such behavior.

The present investigation was undertaken to secure rate data for reaction 1 and to attempt to persuade $HCo(CO)_4$ to behave as a hydride donor in the presence of carbocations.

Results and discussion

Figure 1 shows that reaction 1 is a clean second order reaction; e.g., in the case of the methyl ethyl ketone (MEK)/CH_2Cl_2 (1/4) reaction at 0° C there is a good second order fit through more than five half-lives, curve 5. The reaction is first order with respect to $[HCo(CO)_4]$ and $[Ph_3COH]$. The magnitude of the rate constant increases with solvent polarity; at 0° C in MEK/CH_2Cl_2 (1/1), curve 3, it is more than 200 times that in pure CH_2Cl_2 and in pure MEK the rate is too fast at 0° C to measure conveniently. These data suggest that $Ph_3\overset{+}{C}$ is an intermediate.

The reaction of $Ph_3\overset{+}{C}\overset{-}{B}F_4$ with $HCo(CO)_4$ was investigated in order to determine its rate and stoichiometry. Were the reaction to proceed by hydride abstraction according to eq. 2 one might expect one mol of Ph_3CH to be formed per mol of $HCo(CO)_4$ consumed:

$$Ph_3\overset{+}{C}\overset{-}{B}F_4 + HCo(CO)_4 \rightarrow Ph_3CH + ? \qquad (2)$$

When 1/1 mixture of reactants was used the product consisted (after workup) of a 1/1 mixture of Ph_3CH and Ph_3COH. However when 2 mol of $HCo(CO)_4$ was used, a 100% yield of Ph_3CH was obtained according to eq. 3, probably via steps 3a and 3b (3b corresponds to the combination 1c, 1d, 1e):

$$Ph_3\overset{+}{C}\overset{-}{B}F_4 + HCo(CO)_4 \rightarrow Ph_3CCo(CO)_4 + HBF_4 \qquad (3a)$$

$$Ph_3CCo(CO)_4 + HCo(CO)_4 \rightarrow Ph_3CH + Co_2(CO)_8 \qquad (3b)$$

$$Ph_3CBF_4 + 2HCo(CO)_4 \xrightarrow{k_2} Ph_3CH + Co_2(CO)_8 + HBF_4 \qquad (3)$$

Kinetic measurements on reaction 3, Fig. 1, curve 1, again showed a good second order relationship with a rate constant more than a 1000 times that obtained in the corresponding reaction with Ph_3COH. Apparently simple hydride abstraction by $Ph_3\overset{+}{C}$ does not occur.

Although the reaction of $HMn(CO)_5$ with CF_3SO_3H liberates dihydrogen [4], similar treatment of $HCo(CO)_4$ gave no gas evolution. Of course $HCo(CO)_4$ is a very much stronger acid than $HMn(CO)_5$ and it may require a very much stronger acid than CF_3SO_3H to force $HCo(CO)_4$ to behave as a hydride. Despite the great versatility of $HCo(CO)_4$ [5], there is as yet no evidence that it can function as a hydride donor.

The addition of catalytic quantities of $HBF_4 \cdot Et_2O$ to reaction 1, increased the rate of this reaction (Fig. 1, curve 2), by a factor of more than 1000. This effect is very likely due to the enhancement of the rate of formation of the ion pair shown in eq. 1a. The suggestion of reactions 1c—1e implicating radicals originally proposed in 1953 is now strengthened; in 1982 the first experimental evidence (CIDNP) for the presence of radicals in room temperature stoichiometric reactions with $HCo(CO)_4$ was reported [6].

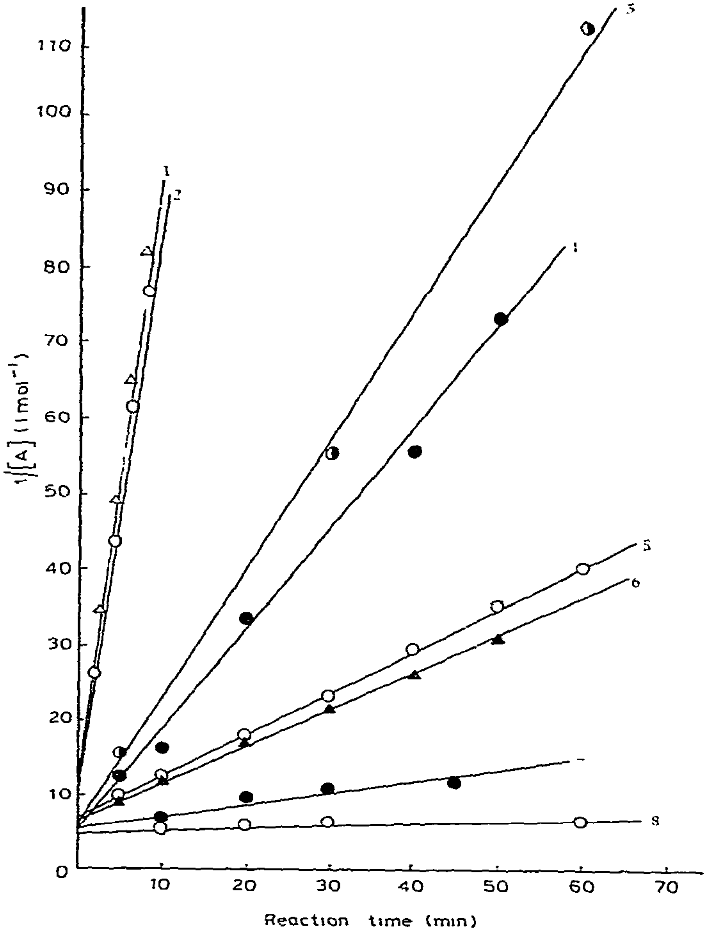

Fig. 1. Second order plots: (k_2 values in l mol^{-1} s^{-1} × 10^2); (1) $Ph_3C \cdot BF_4$ in CH_2Cl_2 at 0°C (7.14); (2) Ph_3COH in CH_2Cl_2 at 0°C (catalytic quantity of $HBF_4 \cdot Et_2O$) (6.81); (3) Ph_3COH in CH_2Cl_2/MEK (1/1) at 0°C (1.45); (4) Ph_3COH in CH_2Cl_2/MEK (2/1) at 0°C (1.10); (5) Ph_3COH in CH_2Cl_2/MEK (4/1) at 0°C (0.475); (6) Ph_3COH in CH_2Cl_2/acetone (4/1) at 0°C (0.425); (7) Ph_3COH in CH_2Cl_2/acetylacetone (4/1) at 0°C (0.135); (8) Ph_3COH in CH_2Cl_2 at 20°C (0.025).

Experimental

Kinetic measurements. The reaction of Ph_3COH with $HCo(CO)_4$ in 4/1 CH_2Cl_2/MEK, which is typical of all kinetic runs, will be described in detail.

To a 10 ml solution of 0.506 *M* $HCo(CO)_4$ [7] in 4/1 CH_2Cl_2/MEK, there was added 2.53 mmol of Ph_3COH in 6 ml of the same solvent under CO at 0°C. Samples were removed periodically and quenched with $H_2NCH_2CH_2NH_2$. The solution was shaken, diluted with cold water, and the organic layer separated, washed, dried, and evaporated to dryness. The residue was dissolved in $CDCl_3$ and ^1H NMR determined from which the ratio of Ph_3COH/Ph_3CH was calculated.

The reaction between $Ph_3\overset{+}{C}\overset{-}{B}F_4$ and $HCo(CO)_4$ (eq. 3) was carried out under CO similarly to the kinetic runs described above. 2,6-Dimethylnaphthalene was used as an internal standard. The $Ph_3\overset{+}{C}\overset{-}{B}F_4$ was prepared according to the literature [8] and was used immediately. After completion of the reaction, the solution was sampled and the IR spectrum showed the presence of $Co_2(CO)_8$. A syringe needle was inserted in the septum (which had sealed the flask) to release any CO. After standing in the open for about 10 min vigorous CO (gas phase IR) evolution occurred and an unstable yellow precipitate separated; it was extremely sensitive to moisture. This precipitate was filtered under CO, washed twice with CH_2Cl_2, and then with pentane. It melted with decomposition at 100—103°C; its ^1H NMR spectrum in CH_3CN showed phenyl protons only and the IR spectrum in CH_3CN showed no carbonyl bands. The IR spectrum of the mull was quite similar to that of $Ph_3\overset{+}{C}\overset{-}{B}F_4$. On shaking a CH_2Cl_2 suspension of the compound with H_2O, the aqueous layer turned the pink color characteristic of Co^{2+}. Evaporation of the CH_2Cl_2 layer gave pure Ph_3COH. We tentatively assign the structure $Ph_3C[Co(BF_4)_3]$ to this compound although the analysis was not completely satisfactory. Found [9]: C, 36.72; H, 3.02; Co, 10.00; F, 31.70; B, 6.11. $C_{19}H_{15}Co_3F_{12}B_3$ calcd.: C, 40.56; H, 2.69; Co, 10.47; F, 40.52; B, 5.76%. In view of the great difficulty in handling this compound and in view of its marginal significance to the major thrust of this work, no further characterization was attempted.

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[9] Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee. The unusual sensitivity toward moisture may be responsible for the unsatisfactory carbon analysis.