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Reaction of cobalt tetracarbonyl hydride with phenylacetylene

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

Abstract

In C_6H_6 or hexane at room temperature, under an atmosphere of CO, excess $HCo(CO)_4$ reacts with phenylacetylene to give ethylbenzene and 2-phenylpropanal, the same products that result from the similar reaction of styrene. This and other evidence show that styrene is an intermediate. However, when phenylacetylene is in large excess, neither ethylbenzene, 2-phenylpropanal, nor styrene is formed in more than trace quantity. Instead, a compound is formed whose spectral properties suggest that it is an alkyl- or acylcobalt carbonyl containing a 1-phenylethenyl group. This compound reacts with $HCo(CO)_4$ to give styrene. CIDNP suggests that the reaction of phenylacetylene with $HCo(CO)_4$ proceeds through radical pairs [1-phenylethenyl··$Co(CO)_4$]. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydroformylation; Phenylacetylene; Styrene; Cobalt tetracarbonyl hydride; Alkenylcobalt carbonyl; CIDNP; Free-radical reaction

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1. Introduction

CIDNP from a reaction of $HCo(CO)_4$ with an alkene (1,1-diphenylethylene) was first reported by Nalesnik and Orchin [1]. This clear evidence of a radical mechanism prompted investigations of related reactions, including those of styrene. In the probe of an NMR spectrometer at ~35°C, reactions of styrene with $HCo(CO)_4$ give ethylbenzene, 2-phenylpropanal, and probably 2-phenylpropanoylcobalt tetracarbonyl with CIDNP consistent with the radical-pair mechanism of Scheme 1 [2]. This raises questions about similar reactions of the analogous alkyne, phenylacetylene.

At high temperatures and pressures of CO, Co-catalyzed reactions of alkynes give saturated aldehydes, usually in low yield [3]. Analogous Rh-catalyzed reactions proceed by initial hydroformylation (syn addition) followed by hydrogenation of the intermediate α,β-unsaturated aldehyde [4].

Our study has several goals: (1) to determine the products of the stoichiometric reaction of phenylacetylene with $HCo(CO)_4$; (2) to determine the order of hydroformylation and hydrogenation, if both occur; (3) to identify intermediates in these reactions; and (4) to explore the possibility of radical-pair mechanisms. Toward these ends, we have examined reactions of phenylacetylene with $HCo(CO)_4$ and $DCo(CO)_4$ using methods similar to those applied to analogous reactions of styrene, involving NMR spectroscopy and CIDNP.

2. Experimental

2.1. Commercial compounds

Perdeuteriobenzene (C_6D_6; Aldrich, Wilmad, or Cambridge; labeled 99.5 at.% D) showed no NMR absorption other than residual C_6D_5H and was used as received. *N*,*N*-Dimethylformamide (DMF) was distilled

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at reduced pressure and stored over molecular sieves (Linde, 4 Å) under nitrogen. Phenylacetylene (Lancaster) was distilled under aspirator pressure and stored under nitrogen in the dark. $Co_2(CO)_8$ was twice recrystallized from hexane.

2.2. Preparation of (2,4,6-trimethylphenyl)acetylene

(2,4,6-Trimethylphenyl)acetylene was prepared by the method of Yates and Madrapilias [5] and redistilled at 98–101°C (8 mm) to give a colorless liquid. IR (neat): 3320, 3200, 2115, 860, 738 cm^{-1}. NMR (CCl_4): δ 6.70 (br s), 2 H), 3.21 (s, 1 H), 2.36 (s, 6 H), 2.19 (s, 3 H) ppm.

2.3. Preparation of phenylacetylene-β-d

The alkynyl H of phenylacetylene was repeatedly exchanged with D_2O, catalyzed by CaO [6], followed by distillation. The resulting phenylacetylene was > 96% β deuterated (^{1}H-NMR).

2.4. Preparation of styrene-β-d [7]

In a foil-covered, 3-necked, 250-ml flask, with ice-bath cooling, Mg (1.3 g, 0.054 mol), β-bromostyrene (Aldrich, mixture of isomers; 3.6 g, 0.021 mol), and ethyl bromide (3.1 g, 0.030 mol) were allowed to react in THF (21 ml). On completion of the reaction and 1 h additional stirring, 2.0 ml (0.11 mol) D_2O in 10 ml THF was added. The organic layer was separated, the aqueous layer extracted three times with 10-ml portions of diethyl ether, and the organic layer and ether extracts combined, dried ($CaCl_2$), stripped of solvent, and distilled under vacuum with a bath temperature less than 70°C, giving 1.2 g (58%) a mixture of *cis*- and *trans*-β-deuteriostyrenes, 17% *cis* and 83% *trans*, according to ^{1}H- and ^{2}H-NMR spectra.

This mixture was used as the starting material for the determination of the time required for the equilibration of *cis*- and *trans*-β-deuteriostyrenes under the influence of $HCo(CO)_4$.

2.5. Preparation, assay, and storage of stock solutions of $HCo(CO)_4$ and $DCo(CO)_4$

$HCo(CO)_4$ solutions in C_6D_6 (for ^{1}H-NMR experiments) or heptane (for ^{2}H-NMR) were prepared under CO by acidifying (cold, concentrated HCl) the product of the reaction of $Co_2(CO)_8$ with DMF [8]; separating the nonaqueous layer; washing it twice with cold, degassed water; pouring it through a column of anhydrous calcium sulfate into a storage vessel that had been evacuated and flushed with CO several times; and storing in a dry-ice-filled Dewar flask.

Concentrations of $HCo(CO)_4$ in stock solutions were determined (a) by titration with 0.1 M aqueous NaOH to a phenolphthalein endpoint, using the average of two titrations, or (b) by integrating ^{1}H-NMR signals for C_6H_6 (added as internal standard, δ 7.15 ppm) and $HCo(CO)_4$ (δ −11.6 ppm) (when the solvent was C_6D_6, the signal of residual C_6D_5H was too weak to interfere). Method (b) was deemed more reliable, due to the difficulty of detecting the titration endpoint. All concentrations used in kinetic studies were determined by NMR.

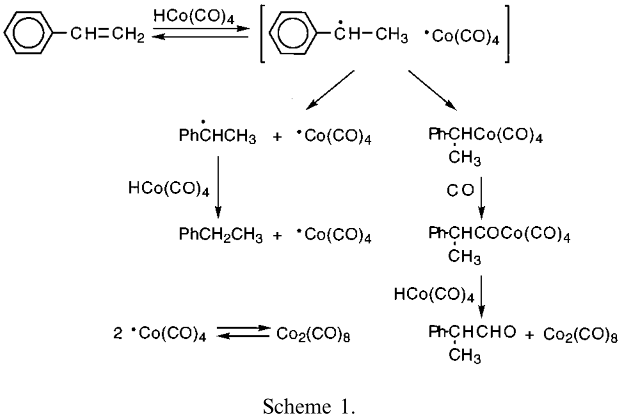
$DCo(CO)_4$ in heptane was made from $HCo(CO)_4$, which was prepared as above (stopping at the initial phase separation). The heptane phase was then twice shaken with D_2O, separated, and further treated in the same manner as $HCo(CO)_4$ (above). The resulting solution showed no absorption at δ −11.6 ppm $[\underline{H}Co(CO)_4]$. Stock solutions were assayed by ^{2}H-NMR using added C_6D_6 as internal standard.

2.6. Preparation of hexacarbonyl(μ-phenylacetylene)-dicobalt [9]

With water-bath cooling as needed, phenylacetylene (1.02 g, 10 mmol) was allowed to react (1 h) with $Co_2(CO)_8$ (3.42 g, 10 mmol) in 25 ml of petroleum ether under CO. The dark red oil remaining after vacuum distillation of the petroleum ether was chromatographed on silica gel (eluted with petroleum ether). After solvent removal, 3.0 g (61%) of hexacarbonyl(μ-phenylacetylene)dicobalt, $(PhC\equiv CH)Co_2(CO)_6$, was obtained. IR (in heptane): 2094.5 (2.4), 2057.4 (10), 2032.0 (8.4), 2027.7 (8.0), 2016 (0.7) cm^{-1} [10]. ^{1}H-NMR (in C_6D_6): δ 7.21 (br s, 5 H), 5.78 (s, 1 H) ppm.

2.7. Preparation of 2-phenylpropenal (atropaldehyde) [11]

A mixture of styrene (57 ml, 0.50 mol), chloroform (50 ml), dichloromethane (25 ml), 50% aqueous NaOH (70 ml), and triethylbenzylammonium chloride (2.0 g;



Scheme 1.

phase-transfer catalyst) was allowed to react, with stirring, until the temperature reached 50°C, when 25 ml additional dichloromethane was added. After stirring for 1 h, the temperature was increased to 60°C and held for an additional 1 h. Cooling, separating the organic layer, extracting of the aqueous layer with diethyl ether, drying the combined organic layers ($MgSO_4$), filtering, concentrating, and distilling led, after a forerun, to 45 g (48%) 1,1-dichloro-2-phenylcyclopropane. B.p.: 105–110°C (8 mm). NMR (CCl_4): δ 7.11 (br s, 5 H), 2.85 (br t, 1 H), 1.65–1.98 (complex m, 2 H) ppm.

1,1-Dichloro-2-phenylcyclopropane (9.3 g, 0.050 mol), ethanol (70 ml), and 50% aqueous NaOH (10 ml) were refluxed for 18 h, poured onto 150 g ice, and extracted three times with 25 ml portions of petroleum ether. The combined extracts were dried, stripped of solvent, and distilled under reduced pressure (oil pump), collecting 5.0 g (fractions boiling 70–100°C (2.0 mm)) of impure diethyl acetal of 2-phenylpropenal. NMR (CCl_4): δ 7.0–7.4 (m, 5 H) ppm, 5.66 (s, 2 H), 5.18 (s, 1H), 3.53 (m, 4 H), 1.18 (t, 6H). Contamination, ~20%, was evident in the NMR spectrum.

After the acetal (5.0 g) was swirled for 60 s at 0°C with a solution of formic acid (5 ml) and water (2 ml), a mixture of water (20 ml) and petroleum ether (10 ml) was added and the aqueous phase was removed with a Pasteur pipette. The combined organic phases (including two 5-ml petroleum-ether extracts of the aqueous phase) were dried ($MgSO_4$), stripped of solvent (rotary evaporator without heat), and dissolved in a mixture of 10 ml petroleum ether and 5 ml diethyl ether. The crystals that formed after 20 min of cooling at -50°C were washed with cold petroleum ether and dried in vacuo, giving 2.2 g (34% from 1,1-dichloro-2-phenylcyclopropane) 2-phenylpropenal. NMR (C_6D_6): δ 9.23 (s, 1 H), 6.8–7.3 (m, 5 H), 6.65 (s, 1 H), 5.05 (s, 1 H) ppm.

2.8. Reactions in an NMR spectrometers (for CIDNP, product spectra, and kinetics)

A sample was prepared in a 5 or 10 mm (outer diameter) NMR tube. The tube was dried overnight in an oven and placed in a side-armed test tube covered with a rubber septum. Through the side arm, the apparatus was evacuated and filled with CO several times, after which the NMR tube was charged (through the septum, using a gas-tight syringe) with stock $HCo(CO)_4$ or $DCo(CO)_4$ solution that had been allowed to warm to room temperature. For ^{1}H-NMR studies, C_6D_6 was the solvent; for ^{2}H-NMR, heptane. An internal standard was added (optionally) at this time (C_6H_6 for $HCo(CO)_4$ in C_6D_6 or heptane; C_6D_6 for $DCo(CO)_4$ in heptane). Under a fast flow of CO, the septum was removed and the NMR tube capped, after which it was kept immersed in a dry-ice bath until used.

For a CIDNP experiment, an NMR tube charged with $HCo(CO)_4$ or $DCo(CO)_4$ solution was allowed to warm to room temperature. The pressure cap was pulled back to allow ingress of a syringe needle and the substrate (neat or in solution) was added down the side of the tube, after which the cap was replaced. Reaction was initiated by vigorous shaking, the tube placed immediately in the probe of the spectrometer (usually a Varian EM-390), and a stopwatch started. The spectral region of interest was scanned repeatedly at 10 ppm min^{-1}. Finally, the entire spectrum was obtained with scanning at a slower rate. The entire experiment lasted about 10 min.

When a Jeol-FX90Q spectrometer was used, its open architecture allowed a slightly different procedure. The charged sample tube was first placed in the probe and a reference spectrum recorded. Substrate (neat or solution) was added to the slightly-withdrawn tube and it was recapped, shaken, and replaced, leaving it between the poles of the magnet at all times during this procedure. The spectrum was recorded and stored at fixed subsequent time intervals.

For ^{2}H-NMR experiments, a Jeol-FX90Q spectrometer was used. The procedure was like that for CIDNP experiments except that a sealed 5 mm tube containing 0.5 ml 4.0 M LiBr in H_2O was placed inside the 10 mm tube containing the sample. The spectrometer was locked on the ^{7}Li signal. During the reaction, ^{2}H-NMR spectra were recorded in sets of 16 transients and stored. Finally, a product spectrum was obtained from 100–400 transients. Where only the product spectrum was desired, the NMR tube was held in a water bath (instead of the probe) until reaction was judged complete.

Kinetic measurements on the reaction of $HCo(CO)_4$ with phenylacetylene used the Jeol-FX90Q NMR spectrometer, solvent C_6D_6, and added internal standard C_6H_6. The procedure above was followed, except that the $HCo(CO)_4$ concentration was measured before adding excess phenylacetylene (molar ratio $PhC{\equiv}CH{:}HCo(CO)_4$ of 3–14) and initiating the reaction. Spectra were recorded as sets of four transients at 36 s intervals. $HCo(CO)_4$ was monitored by its signal at δ -11.6 ppm (normalized by the signal from C_6H_6). Three runs of varying concentrations of $HCo(CO)_4$ gave consistent results when fitted using a second-order plot.

Similar procedures were used to determine the time required for the equilibration of *cis*- and *trans*-β-deuteriostyrenes under the influence of $HCo(CO)_4$.

3. Results and discussion

^{1}H-NMR spectra of product solutions from reactions of phenylacetylene with excess $HCo(CO)_4$ reveal

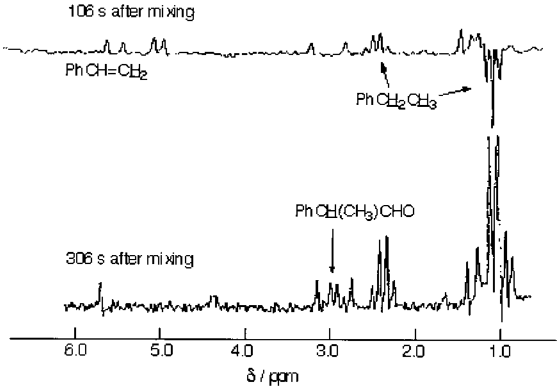
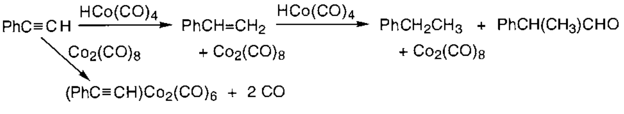


Fig. 1. ^1H-NMR spectra of a mixture of phenylacetylene and $HCo(CO)_4$ in C_6D_6 at ambient (room and probe) temperatures. $[PhC{\equiv}CH]_0 = 0.075$ M. $[HCo(CO)_4]_0 = 0.21$ M.

$PhCH_2CH_3$, $PhCH(CH_3)CHO$, and $(PhC{\equiv}CH)Co_2(CO)_6$ [hexacarbonyl(μ-phenylacetylene)dicobalt] (Fig. 1). The latter is represented by a singlet at δ 5.78 ppm, identical with that of authentic $(PhC{\equiv}CH)Co_2(CO)_6$. Aside from $(PhC{\equiv}CH)Co_2(CO)_6$, a product of a reaction of $PhC{\equiv}CH$ with $Co_2(CO)_8$, these are the products of the reaction of styrene with $HCo(CO)_4$, suggesting that styrene is an intermediate in a two-stage process (Scheme 2): (1) reduction (hydrogenation) of $PhC{\equiv}CH$ to $PhCH{=}CH_2$; (2) reaction of $PhCH{=}CH_2$ through the usual radical-pair pathway (Scheme 1).

This is amply confirmed by additional evidence. (1) The NMR yield ratio $(PhCH(CH_3)CHO)/(PhCH_2CH_3)$ is 39/62 (0.63) from $PhC{\equiv}CH$ ($[PhC{\equiv}CH]_0$, 0.082 M; $[HCo(CO)_4]_0$, 0.20 M) and 28/73 (0.38) from $PhCH{=}CH_2$ ($[PhCH{=}CH_2]_0$, 0.15 M; $[HCo(CO)_4]_0$, 0.20 M). The difference is marginally outside experimental error, if at all. (2) The products exhibit CIDNP [Fig. 1; $PhC\underline{H}_2CH_3$, A; $PhCH_2C\underline{H}_3$, E; $PhC\underline{H}(CH_3)CHO$, E (very weak); A = enhanced absorption, E = emission]. CIDNP with these phases is also found in products of reactions of styrene with $HCo(CO)_4$. The enhanced absorption in $PhC\underline{H}_2CH_3$ is more clearly seen here than for the styrene reaction. (3) Styrene signals appear as transients (Fig. 1) when $HCo(CO)_4$ is in large excess. (4) Styrene is a major product when its (NMR) yield is maximized (molar ratio $HCo(CO)_4{:}PhC{\equiv}CH \approx 1{:}1$). (5) The small amount of $PhCH{=}CH_2$ that is formed in the reaction of $HCo(CO)_4$ with excess $PhC{\equiv}CH$ exhibits CIDNP. Within the first few seconds of reaction, doublets at δ 5.0 and 5.5 ppm ($PhCH{=}C\underline{H}_2$) are seen in emission (Fig. 2). These signals rapidly weaken and disappear.



Scheme 2.

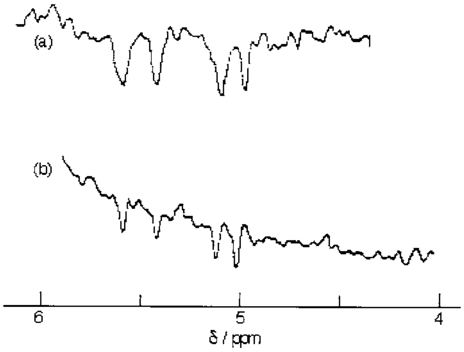


Fig. 2. CIDNP in styrene formed in the reaction of phenylacetylene or phenylacetylene-β-d with $HCo(CO)_4$ in C_6D_6 at ambient temperatures. (a) $[PhC{\equiv}CH]_0 = 1.45$ M. $[HCo(CO)_4]_0 = 0.17$ M. (b) $[PhC{\equiv}CD]_0 = 1.5$ M. $[HCo(CO)_4]_0 = 0.15$ M; 104 s after mixing.

From the reaction of $HCo(CO)_4$ with a large excess of $PhC{\equiv}CH$, $PhCH{=}CH_2$, $PhCH_2CH_3$, and $PhCH(CH_3)CHO$ are nearly absent (barely detectable at best). The detection of $PhCH{=}CH_2$ is assisted by CIDNP, while it lasts.

Under these conditions, the major product is **X**, which exhibits ^1H-NMR singlets at δ 2.8 and 3.3 ppm. With less intensity, these signals appear even when $PhC{\equiv}CH$ is not in large excess (Fig. 1). They are broad singlets in ^2H-NMR spectra of products of reactions of $PhC{\equiv}CD$ with $HCo(CO)_4$ (Fig. 3), suggesting that **X** is an organometallic compound, which may give broad peaks in ^2H-NMR spectra due to quadrupolar interactions of ^2H with electric field gradients. Attempts to prove the structure of **X** have led to a plausible hypothesis but not a confirmed conclusion (see later).

Since **X** is only a minor product when $HCo(CO)_4$ is in excess, it appears to be an intermediate in the overall reaction. If so, the mechanism can be elaborated [omitting, for clarity, the formation of $(PhC{\equiv}CH)Co_2(CO)_6$] as follows.

$$PhC{\equiv}CH \xrightarrow{HCo(CO)_4} \mathbf{X} \xrightarrow{HCo(CO)_4} PhCH{=}CH_2 \xrightarrow{HCo(CO)_4}$$

$$PhCH_2CH_3 + PhCH(CH_3)CHO$$

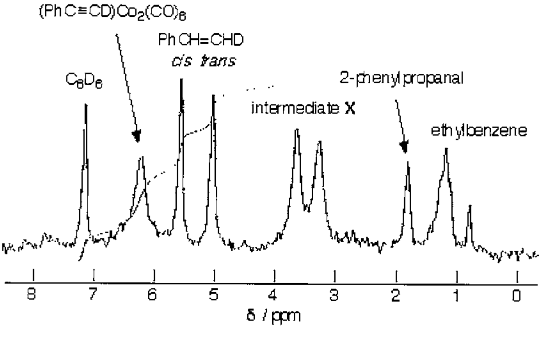


Fig. 3. ^2H-NMR spectrum of a mixture of phenylacetylene-β-*d* and $HCo(CO)_4$ in heptane five minutes after mixing reactants at ambient room temperature. $[PhC{\equiv}CD]_0 = 0.52$ M. $[HCo(CO)_4]_0 = 0.50$ M.

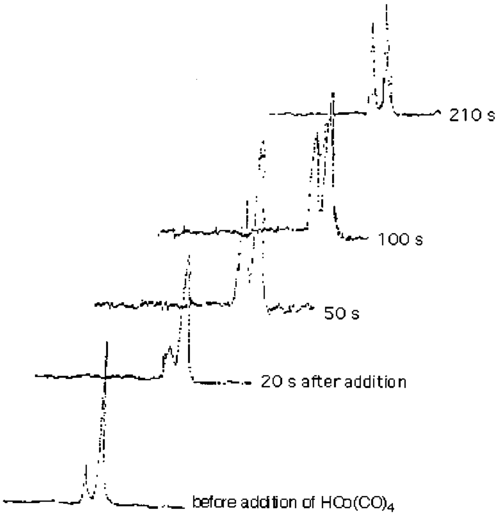


Fig. 4. ^{2}H-NMR traces for the $HCo(CO)_4$-catalyzed isomerization of β-deuteriostyrene in heptane at ambient NMR probe temperature. *cis*-β-Deuteriostyrene (left): δ 5.5 ppm. *trans*-β-Deuteriostyrene (right): δ 5.0 ppm. $[\text{styrenes}]_0 = 0.77$ M. $[HCo(CO)_4]_0 = 0.22$ M.

To probe the stereochemistry of the hydrogenation of PhC≡CH to $PhCH{=}CH_2$, we carried out reactions of PhC≡CD with $HCo(CO)_4$ and of PhC≡CH with $DCo(CO)_4$. Both gave equimolar mixtures of *cis*- and *trans*-β-deuteriostyrene (with the α position deuterated as well in the latter case). ^{2}H-NMR spectra taken at periods during the reaction indicate that it is non-stereoselective at all stages. Thus, the hydrogenation is not analogous to the Rh-catalyzed reaction, where *syn* hydroformylation occurs [4].

The observed nonstereoselectivity of hydrogenation could be a consequence of isomerization of PhCH=CHD by $HCo(CO)_4$. Indeed, such isomerization does occur (Fig. 4). However, full equilibration under the conditions of our reactions takes about five min, whereas we observed the nonstereoselective formation of PhCD=CHD within seconds of the initiation of the reaction of PhC≡CH with $DCo(CO)_4$. Thus, hydrogenation itself is nonstereoselective.

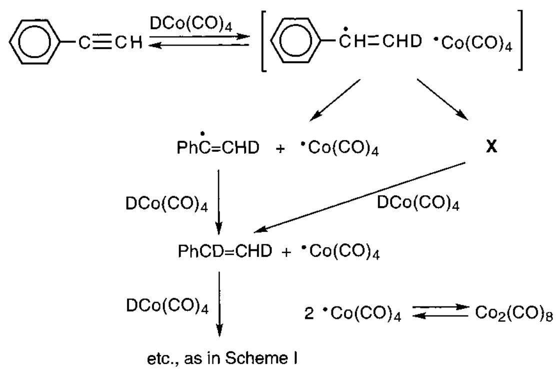
Both CIDNP in $PhCH{=}CH_2$ and the nonstereoselective formation of PhCH=CHD would be expected if the reaction of PhC≡CH with $HCo(CO)_4$ followed a mechanism parallel with that of $PhCH{=}CH_2$ (Scheme 3, illustrated for $DCo(CO)_4$).

This mechanism is further supported by the ^{2}H-NMR spectrum of **X**-*d* and the ^{1}H-NMR spectrum of **X**. Whether **X**-*d* is formed from PhC≡CD and $HCo(CO)_4$ or from PhC≡CH and $DCo(CO)_4$, the ^{2}H-NMR peaks at δ 2.8 and 3.3 ppm are of equal intensity. This would be expected if D were partitioned with equal probability between nonequivalent sites, perhaps *cis*/*trans*, in **X**. **X** also exhibits singlets of equal intensity at δ 2.8 and 3.3 ppm, consistent with a moiety $PhC(Z){=}CH_2$, where Z is the remainder of the molecule. The singlets are consistent with the absence of an α-H, a typical chemical shift difference of about 0.5 ppm between the methylene protons $PhC(Z){=}C\underline{H}_2$, and a typically small geminate coupling constant between these protons. Their chemical shifts are distinctly upfield, however, from styrene itself (δ 5.0 and 5.5 ppm), indicating that if **X** is $PhC(Z){=}CH_2$, then Z exerts a pronounced shielding effect.

The CIDNP phase of $PhCH{=}C\underline{H}_2$ also supports Scheme 3. Kaptein's Rule for net effects is: sign of net effect $= \mu \times \varepsilon \times \Delta g \times a(\text{i})$, where the sign of the net effect is $(-)$ for E and $(+)$ for A, μ is $(+)$ for an initially triplet or $(-)$ for an initially singlet radical pair, ε is $(+)$ for a product of geminate reaction and $(-)$ for a product of radical-pair escape, Δg is the sign of the difference g(radical containing the proton being observed) $- g$(other radical), and a(i) is the sign of the hyperfine coupling constant between the proton being observed and the unpaired electron of the radical in which it resides in the radical pair. For styrene formed according to Scheme 3, $\mu = (-)$ (singlet pair), $\varepsilon = (-)$ (escape product), $\Delta g = (-)$ $\{g[PhC(^{\bullet}) = CH_2] < g[^{\bullet}Co(CO)_4]\}$, and $a(\text{i}) = (+)$ (β-proton, $^{\bullet}$C–C–H). The product of these signs is $(-)$; *E* is predicted for $PhCH{=}C\underline{H}_2$, as observed (Fig. 2).

The observed *E* for $PhCH{=}C\underline{H}_2$ is not due to reversal of the radical-pair forming step of its reaction with $HCo(CO)_4$ (Scheme 1). This would give A instead (opposite from the observed E for $PhCH_2C\underline{H}_3$, an escape product in Scheme 1, because $PhCH{=}CH_2$ is a product of geminate reaction).

Interestingly, CIDNP is not seen when there is enough $HCo(CO)_4$ present to convert most of the PhC≡CH into styrene and $(PhC{\equiv}CH)Co_2(CO)_6$. CIDNP is a nuclear spin selection process in which different nuclear spin states preferentially send radical intermediates into geminate reaction or escape products. In this case, $PhCH{=}CH_2$ is an escape product and **X** is presumed to be a geminate reaction product. If **X** is converted rapidly into $PhCH{=}CH_2$ (presumably, in this case, in a reaction of **X** with $HCo(CO)_4$), then



Scheme 3.

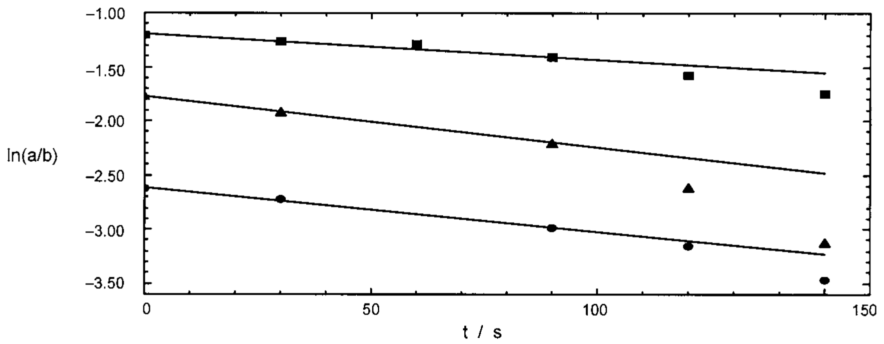


Fig. 5. Second-order plots for reactions of PhC≡CH (excess) with $HCo(CO)_4$ in C_6D_6 at 29°C. $a = [HCo(CO)_4]$. $b = [PhC{\equiv}CH]$. $[PhC{\equiv}CH]_0 = 1.40$ M. Run 1: $[HCo(CO)_4]_0 = 0.102$ M; $k = 3.2 \times 10^{-3}$ M^{-1} s^{-1}. Run 2: $[HCo(CO)_4]_0 = 0.238$ M; $k = 4.1 \times 10^{-3}$ M^{-1} s^{-1}. Run 3: $[HCo(CO)_4]_0 = 0.422$ M; $k = 2.4 \times 10^{-3}$ M^{-1} s^{-1}. Average value of k: 3×10^{-3} M^{-1} s^{-1}.

$PhCH{=}CH_2$ becomes a product of both escape and geminate reaction and spin selection is undone, cancelling any CIDNP that might have been generated in escape and geminate reaction products separately.

The rate law implied by Scheme 3 is complex, but when PhC≡CH is in excess, an initial second-order rate law, first-order in $HCo(CO)_4$ and PhC≡CH, may obtain. Provided that **X** is the major product, so that the $HCo(CO)_4$ and PhC≡CH are consumed in equal amounts, the usual integrated second-order rate law for this case may apply. One form is given by Eq. (1), where a and b are the concentrations of $HCo(CO)_4$ and PhC≡CH, respectively, subscript zeroes denote initial values, t is time, and k is the second-order rate constant.

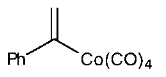
$$\begin{aligned}\ln(a/b) &= \ln\{a/[b_0 - (a_0 - a)]\}\\ &= -(b_0 - a_0)kt + \ln(a_0/b_0) \qquad (1)\end{aligned}$$

Fig. 5 shows corresponding plots of kinetic data.

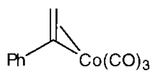
After about 90 s, points deviate significantly from straight lines fitted to the first few points. This corresponds to the approximate time at which evolution of gas (presumably CO) becomes noticeable, suggesting that significant amounts of $Co_2(CO)_8$ have been formed and that its reaction with PhC≡CH is occurring. The rate constants derived from initial rates are similar for three runs (Fig. 5) and do not show a trend with $[HCo(CO)_4]_0$. Therefore we consider that the data conform to the mechanism of Scheme 3.

To help identify **X**, we obtained the IR spectrum of a mixture of PhC≡CH and $HCo(CO)_4$ (molar ratio ~ 14:1) in heptane 20 min after mixing at 15°C. Absorption bands not belonging to reactants or anticipated products appeared at 2081.5 (s), 2072 (s), 2024 (vs, br), 1834 (m, br) cm^{-1} (spectrometer: Carl Zeiss Jena IR 75). The broad band at 1834 cm^{-1} may reflect a strained carbonyl group [compare the bridging carbonyl stretches of $Co_2(CO)_8$ at 1866 and 1856 cm^{-1}]. A similar IR absorption was reported by Heck for the product of the reaction of crotonyl chloride with $NaCo(CO)_4$ in ether and was ascribed to a π-crotonylcobalt tricarbonyl [12].

Candidates for **X** include **1**–**4**, of which **1** and **2** are alkenylcobalt carbonyls. Alkenylcobalt carbonyl intermediates have been postulated for butenolide syntheses from acylcobalt tetracarbonyls and alkynes [13,14]. A few perfluoroalkenylcobalt carbonyls [15–18] and phosphine-substituted alkenylcobalt complexes [19,20] are known.



1



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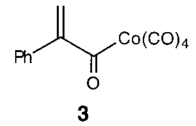
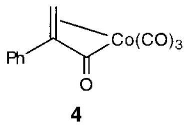


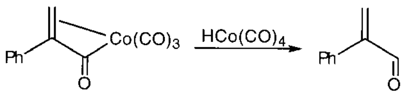
3



4

A substantial upfield chemical shift on complexing an olefinic ligand is characteristic of organometallic compounds containing π-alkenyl metal complexing, suggesting that **X** is **2** or **4**. If the IR band at 1834 cm^{-1} belongs to **X**, then **4** is the most likely structure.

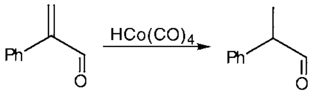
If **X** is **4**, then the most likely primary product of its reaction with $HCo(CO)_4$ is not styrene but is instead 2-phenylpropenal (atropaldehyde). Similar reductive cleavages are typical reactions of acyl cobalt carbonyl complexes [21].



However, it is possible that the alkenylcobalt carbonyls **1** and **2** and the acylcobalt carbonyls **3** and **4** equilibrate and that **1** or **2** is more reactive toward $HCo(CO)_4$ than **3** and **4**. This would provide a plausible mechanism for the conversion of **X** to styrene, even if **4** dominated at equilibrium (so that its spectral properties were observed).

$$\mathbf{4} \rightleftarrows (\mathbf{1} \text{ or } \mathbf{2}) \xrightarrow{HCo(CO)_4} PhCH=CH_2$$

Even so, 2-phenylpropenal cannot be ruled out as an intermediate. Its signals have not been detected in the NMR spectra of reaction mixtures, but in control experiments, we find that the reaction of 2-phenylpropenal with $HCo(CO)_4$ is so fast that it is complete on mixing (as shown by ^{1}H-NMR spectra). Therefore the failure to detect 2-phenylpropenal is not significant. The sole product detected by ^{1}H-NMR spectroscopy is 2-phenylpropanal, which is formed without detectable CIDNP.



If there is a pathway through 2-phenylpropenal, then different partitionings between 2-phenylpropanal and ethylbenzene would be expected for reactions of phenylacetylene and styrene with $HCo(CO)_4$, with the reaction of phenylacetylene giving relatively more 2-phenylpropanal. The observed yield ratios $(PhCH(CH_3)CHO)/(PhCH_2CH_3)$, 0.63 from $PhC{\equiv}CH$ and 0.38 from $PhCH{=}CH_2$, vary in the predicted direction, but the effect, if real, is small, reflecting a variation of only 11% in the relative yield of 2-phenylpropanal.

In the hope that the hindered substrate (2,4,6-trimethylphenyl)acetylene would give an intermediate **X**′ that might be better characterized, its reactivity toward $HCo(CO)_4$ was examined. In two hours at room temperature, in C_6H_6 under CO, there was no detectable reaction.

4. Conclusions

A compound (or set of compounds) **X** is formed in the reaction of excess phenylacetylene with $HCo(CO)_4$. Chemical and physical evidence suggest that **X** is a alkenylcobalt carbonyl (1 or 2) or a related acylcobalt carbonyl (3 or 4) containing the 1-phenylethenyl group. Concomitantly with **X**, small amounts of styrene are formed, with CIDNP indicating a radical mechanism and consistent with Scheme 3. When $HCo(CO)_4$ is in excess, **X** reacts further to give styrene, which reacts with $HCo(CO)_4$ through a previously established radical mechanism (Scheme 1), giving ethylbenzene and 2-phenylpropanal as ultimate products.

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