

## Catalytic Homogeneous Hydrogenation of Arenes.

4.<sup>1</sup> Characterization of the Basic Reaction and the Catalysts

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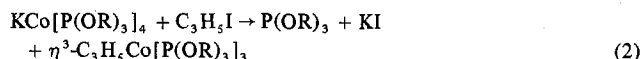
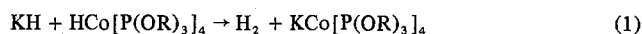
Benzene hydrogenation was catalytically effected at 20 °C and ~1 atm with a series of  $\eta^3$ -allylcobalt(I) complexes of the form  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>CoL<sub>3</sub> with L representing a phosphine or phosphite ligand. All these systems were homogeneous; the reaction media were clear orange solutions. There was a surprising and significant competition in the catalytic hydrogenation between benzene and terminal (1-hexene) olefins with rates that were nearly equal for benzene and for the olefin for one of the allylcobalt catalysts. With  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> as the catalyst, C<sub>6</sub>D<sub>6</sub> + 3H<sub>2</sub> yielded *all-cis*-C<sub>6</sub>D<sub>6</sub>H<sub>6</sub> showing a stereoselective mode of hydrogen addition to the arene ring. Competitive with the hydrogenation reaction was the cleavage of the allyl-cobalt bond with formation of propene and a cobalt hydride that was inactive as a catalyst for arene hydrogenation. Substitution of other, bulkier phosphites or phosphines for the trimethyl phosphite ligand generally led to increased catalyst activity. Activity order for  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>CoL<sub>3</sub> was L = P(OCH<sub>3</sub>)<sub>3</sub> < P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> < P(CH<sub>3</sub>)<sub>3</sub> < P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>. However, this desirable change was uniformly accompanied by a decrease in catalyst life.  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co(CO)<sub>3</sub> was completely inactive as an arene hydrogenation catalyst at 25 °C which is attributed to the relatively higher activation energy for CO dissociation and the lower electron density on the cobalt atom in this complex with respect to the corresponding situations in the phosphite- and phosphine-substituted analogues. ONCo[POC<sub>3</sub>H<sub>7</sub>]<sub>3</sub> also proved inactive as a catalyst for the benzene hydrogenation reaction.

## Introduction

Recently we described<sup>2</sup> the first discrete soluble coordination catalyst,  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, which catalyzed the hydrogenation of benzene and other aromatic hydrocarbons. Additionally, it was reported that this catalyst displayed an unusual selectivity for arenes with respect to simple olefins<sup>3</sup> and a stereochemical feature<sup>1</sup> that comprised addition of the hydrogen atoms solely to one face of the arene molecule. Prior to these preliminary communications, claims to homogeneous catalysis of arene hydrogenation had been advanced<sup>4-8</sup> although discrete complexes were not defined nor was the homogeneity of the system satisfactorily demonstrated throughout the catalytic reaction. For example, Khidekel and co-workers have described an amorphous black rhodium complex with phenylanthranilic acid which gave a black rhodium mixture that catalytically hydrogenated benzene.<sup>4-6</sup> Black uncharacterized reaction mixtures of transition metal carboxylates reduced with trialkylaluminum also catalyzed arene hydrogenation at relatively extreme conditions of temperature (150–210 °C) and pressure (~70 atm).<sup>7,8</sup> Cobalt octacarbonyl has been shown to form in the presence of H<sub>2</sub> and CO at elevated temperature and pressure a homogeneous catalyst for the hydrogenation of polyaromatic hydrocarbons.<sup>9</sup> However, the catalyst was reported to be inert for benzene reduction, although recent workers have predicted that at least slight catalytic activity should be detectable.<sup>10</sup> The well-characterized nature of our allylcobalt complex, which catalyzed significant benzene hydrogenation in pale orange translucent solutions, presents a sharp contrast to the earlier studies and provides a unique opportunity for detailed studies of the role of the transition metal complex as a catalyst in benzene reduction and for considerable insight into the overall mechanism of this reaction. We present here an account of the synthesis and characterization of a number of structurally related complexes which form a series of homogeneous catalysts for arene hydrogenation. The reaction of the allylcobalt complexes with hydrogen has been studied in both inert and aromatic solvents. The experimental conditions for the catalytic reaction are delineated, and the complexes are compared with respect to their catalytic efficiencies and lifetimes. The selectivity feature of the catalyst for arene vs. olefin hydrogenation, now examined in detail, is shown to be competitive at best, not slightly selective as originally reported.<sup>3</sup> The subjects of reaction scope and reaction mechanism will be discussed, shortly, in subsequent papers.

## Discussion

**Synthesis of Allylcobalt Complexes.** A uniform synthesis of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>CoL<sub>3</sub> complexes was not achieved. The methyl and ethyl set of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OR)]<sub>3</sub> complexes were prepared in a high yield by a two step process<sup>11</sup> starting with the easily prepared<sup>11</sup> hydrides HCo[P(OR)]<sub>3</sub> as shown in (1) and (2).



Because the analogous hydride, HCo[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>4</sub>, proved unreactive toward KH,  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub> was prepared by an alternative sequence culminating in the metathesis of allyllithium and ClCo[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub>.<sup>12</sup> The tris(trimethylphosphine) complex was obtained from an analogous sequence. Ligand exchange between P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> in a polar medium provided the preparation of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>. Purification of these allylcobalt complexes by chromatography or recrystallization was an essential step because free phosphite or phosphine ligand substantially reduced the rate of catalytic hydrogenation of arenes.

A full structural characterization of an  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>CoL<sub>3</sub> species has not been achieved and a search for single crystals appropriate for crystallographic studies continues. The <sup>1</sup>H NMR data for the allylcobalt complexes (see Experimental Section) showed in each case an A<sub>2</sub>M<sub>2</sub>X pattern for the allyl ligand. At room temperature the molecules were fluxional, and coupling of the allyl protons with three equivalent phosphorus nuclei was observed. Low-temperature <sup>31</sup>P NMR data<sup>11</sup> established for the complex  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> a limiting stereoisomeric form<sup>11</sup> with two phosphite environments. This stereoisomeric form was stereochemically nonrigid with an E<sub>a</sub> for the AB<sub>2</sub> → A<sub>3</sub> transition in the <sup>31</sup>P NMR spectra of about 9 kcal/mol. There was no evidence<sup>11</sup> up to 110 °C for an  $\eta^3 \rightleftharpoons \eta^1$  allylcobalt form interconversion, a common process in such complexes, that was rapid on the NMR time scale. Such an interconversion is believed to be essential to the catalytic sequence<sup>2,3</sup> but not to be a rate determining step.

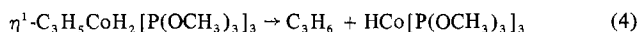
NMR studies showed no evidence of fast phosphite ligand dissociation to 100 °C for  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>; hence phosphite dissociation in this allylcobalt complex must have a forward rate constant that is less than ~10<sup>2</sup> s<sup>-1</sup> at 100 °C. Fast phosphite ligand dissociation in  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub> was detected by <sup>1</sup>H NMR and exchange studies.

Broadening (reversible) of the allyl multiplets ( $J_{H-H}$  and  $J_{H-P}$ ) ensued at  $\sim 80^\circ\text{C}$ ; above  $80^\circ\text{C}$  irreversible decomposition became a fast process. These data suggest a fast Co-P bond-breaking process ( $k_{80^\circ\text{C}} \approx 30\text{ s}^{-1}$ ). Consistent with this hypothesis, addition of  $\text{P}(\text{OCH}_3)_3$  to a solution of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$  showed (NMR) the immediate appearance of free triisopropyl phosphite.

**Reaction of Allylcobalt Complexes with Hydrogen.** In an inert, nonaromatic solvent,  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$  reacted with hydrogen (eq 3) to form a hydride that by our initial



NMR studies was formulated as six-coordinate  $\eta^1\text{-C}_3\text{H}_5\text{CoH}_2[\text{P}(\text{OCH}_3)_3]_3$  with a facial arrangement of allyl and hydrogen atoms. A fully anticipated reaction mode for this hydride complex is a hydrogen (metal hydride) atom transfer to the allyl group to yield propene and, at least transitorily,  $\text{HCo}[\text{P}(\text{OCH}_3)_3]_3$  as depicted in (4). This re-



action was indeed observed; propene was identified in the reaction systems by GC-MS analysis.  $\text{HCo}[\text{P}(\text{OCH}_3)_3]_3$  was not isolated. The only cobalt complex definitively identified from the reaction of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$  with hydrogen has been the very stable and catalytically inactive  $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ . Another cobalt complex was formed, as stoichiometry demands, but purification and identification attempts were unsuccessful; the unidentified cobalt complex was insoluble in conventional solvents. These same essential features were observed with the other allyl analogues although variations in the rate of (4) were observed. With the complex  $\eta^3\text{-C}_6\text{H}_5\text{CH}_2\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ ,<sup>11</sup> which involves a variation in the allylic ligand, rate of benzyl group cleavage was about an order of magnitude higher than the rate of allyl cleavage in  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ . Toluene,  $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ , and a second insoluble cobalt species were the products of the reaction. Allyl cleavage rates comparable to that of the  $\eta^3\text{-benzylcobalt}$  complex were also observed for  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{CH}_3)_3]_3$  and  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$ . The reaction of the latter complex was unique among the series of compounds studied in that propene formation was attendant with the formation of a single cobalt species. The product was isolated and characterized as  $\text{H}_3\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$ .<sup>12</sup>

The allylcobalt complexes also undergo reactions 3 and 4 in *aromatic* solvents, and these reactions have important implications for the catalytic hydrogenation of benzene. The dihydride produced in (3) is an important precursor to the active catalyst and it will be discussed in more detail in a subsequent paper on reaction mechanism. In aromatic solvents propene formation occurred at a reduced rate for each complex relative to its decomposition rate in an inert solvent. This decomposition correlated with the loss of catalytic activity with time. The presence of the arene did not alter the nature of the decomposition products discussed above. The limitations in the catalyst lifetimes resulting from the elimination of propene are discussed below.

**The Catalytic Reaction.** In the presence of  $\eta^3\text{-C}_3\text{H}_5\text{CoL}_3$ , hydrogen and benzene were converted to cyclohexane at  $20^\circ\text{C}$  and  $\sim 1$  atm. Typically, benzene was employed as solvent and reactant. Under these conditions, the reaction medium was a clear orange solution; addition of hydrogen to the reaction system elicited a visible color transition from yellow to orange. Intermediate hydrogenation products, cyclohexene and cyclohexadiene, were not detected unless hydrogen was in a significant deficiency (very low partial pressures) although cyclohexene was generally a dominant product in competitive reactions between benzene and olefins (vide infra). Separation of solid material from the reaction medium was evident only after long reaction times; and at such stages, catalytic activity

**Table I.** Relative Rates of Benzene Hydrogenation Catalyzed by Allyl Derivatives of Cobalt at  $20^\circ\text{C}$  and 1 Atm  $\text{H}_2$

$\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$	1	$\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$	30
$\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OC}_2\text{H}_5)_3]_3$	2	$\eta^3\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$	0
$\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_2\text{-P}(\text{O-}i\text{-C}_3\text{H}_7)_3$	4	$\text{ONCo}[\text{P}(\text{OC}_2\text{H}_5)_3]_3$	0
$\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{CH}_3)_3]_3$	5		

for arene hydrogenation was very low.

Hydrogenation of  $\text{C}_6\text{D}_6$  with hydrogen in the presence of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$  gave  $\text{C}_6\text{D}_6\text{H}_6$  as the only detectable product,<sup>2</sup> and as reported earlier,<sup>1</sup> this product was *all-cis*-cyclohexane-*d*<sub>6</sub> in at least 90% purity (NMR analysis).

**Reactivity of the Allylcobalt Catalysts in the Hydrogenation of Benzene.** Under mild conditions of  $\sim 20^\circ\text{C}$  and  $\sim 1$  atm pressure (see Experimental Section), each molecule of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$  effected 15 cycles of benzene to cyclohexane in about 24 h. All other allylcobalt complexes with phosphorus-based ligands were more active than the trimethyl phosphite derivative. Percentage conversions of benzene to cyclohexane were determined by NMR for 0.1 M solutions of each catalyst after 3- and 24-h intervals. On this basis comparative rate data normalized to those of the trimethyl phosphite complex were established and are listed in Table I. In the phosphite subset of complexes, the only variant is the steric bulk of the alkyl substituent on the phosphite oxygen atom. Clearly, the catalytic activity in this subset fully correlates with the steric bulk of these ligands. In a mechanistic extrapolation, it seems eminently plausible to suggest that catalytic activity correlates with the ease of ligand dissociation in the phosphite complex since there is a general correlation between ligand dissociation and ligand bulk, in an electronically analogous set, for transition metal complexes.

Catalyst life was limited and varied with substituents on the allyl group and the nature of the phosphorus ligand. Under the experimental conditions specified, solutions of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$  under a hydrogen atmosphere retained significant catalytic activity for 48 h. After this time discoloration and separation of solids began to be apparent. The catalysts with triethyl phosphite and mixed phosphite ligands had roughly similar lifetimes. A high degree of activity in a catalyst is often accompanied by a lifetime that is shorter than those of less active, close analogues. This allyl-cobalt system is no exception to this seemingly perverse yet explicable phenomenon. The very high activity of  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$  in benzene hydrogenation was unfortunately accompanied by a short lifetime—a lifetime that was less than one-tenth that of the least active catalyst,  $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ .

The cobalt hydride complexes which were isolated from the spent catalytic systems (vide supra),  $\text{HCo}[\text{P}(\text{OR})_3]_4$  and  $\text{H}_3\text{Co}[\text{P}(\text{O-}i\text{-C}_3\text{H}_7)_3]_3$ , were shown to be completely inactive as catalysts for benzene hydrogenation. Analogous  $\text{H}_3\text{CoL}_3$  complexes were also prepared and tested as catalysts for this reaction. These included  $\text{H}_3\text{Co}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ ,  $\text{H}_3\text{Co}[\text{P}(\text{C}_2\text{-H}_5)_3]_3$ , and a Co(II) analogue,  $\text{H}_2\text{Co}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ . All were inactive catalysts for benzene hydrogenation.<sup>13</sup> Other well-known and very active coordination hydrogenation catalysts for olefin hydrogenation were found inactive in the benzene hydrogenation reaction. At this point in our study of catalytic hydrogenation of benzene in a homogeneous mode it would seem that an allyl ligand (or an analogous ligand capable of facile  $x$  electron donor  $\rightleftharpoons$   $x - 2$  electron donor transformation) is a necessary but not sufficient requirement for a coordination catalyst for arene reduction. Further requirements would appear to be a relatively high electron density on the metal atom, to facilitate addition of the hydrogen molecule, and a low activation energy for ligand dissociation, both of which are realized with phosphite or phosphine ligands. From a

practical point, however, this type of system is mechanistically flawed in that a key intermediate,  $C_3H_5CoH_2L_3$ , can readily follow a reaction path that leads to propene elision and formation of a hydride that is inactive as an arene hydrogenation catalyst. A superior catalytic complex would have an  $\eta^x$  or a redox ligand, subject to a facile conversion to an  $\eta^{x-2}$  form or electron transfer between metal and ligand, that would not be susceptible to an H-ligand elision; in principle  $ONCoL_3$  would meet these conditions. However, we found  $ONCo[P(OC_3H_7)_3]_3$  to be inactive as a catalyst for benzene hydrogenation.<sup>12</sup>

**Selectivity of the Catalytic Reaction.** The catalyzed hydrogenations of equimolar mixtures of benzene and 1-hexene resulted in the formation of the saturated products *n*-hexane and cyclohexane; in addition, a significant amount of cyclohexene was produced. The relative amounts of these products produced were sensitive to the substituent ligand on the cobalt catalyst and to the duration of the hydrogenation. Analysis of the reduction products at different time intervals indicated that the relative amounts of *n*-hexane increased with time. This increased rate of olefin hydrogenation is attributed to the catalytic activity of the trihydride  $H_3CoL_3$ , which was produced during the course of a hydrogenation reaction. This olefin hydrogenation catalyst is expected to be formed in at least trace amounts whenever the allyl derivative is subjected to hydrogen pressure. The presence of this second catalytic species, which was active *only* for olefin hydrogenation, made difficult the determination of the true selectivity of  $C_3H_5CoL_3$  for arene hydrogenation vs. that of olefins. Within this limitation, however, truly competitive hydrogenations of the arene and olefin have been established although the initially observed selectivity ratios which favored arene reduction have not been reproduced. Ratios of cyclohexene-cyclohexane: hexane as high as 7:10 were observed with the triisopropyl phosphite derivative after short periods of time (e.g., 1–2 h). This ratio was lower, ~3:10, with the complex containing trimethyl phosphite ligands.

Only cyclohexane was observed when benzene was catalytically hydrogenated in the absence of other substrates. The all-*cis* stereochemistry of the hydrogenated arene indicated a strong interaction of the arene with the catalyst and complete reduction of the molecule while it retained a single gross orientation with respect to the metal ion. However, a linear olefin is expected to compete effectively for the catalytic site during the final step in the hydrogenation process which involves the interaction of a cyclohexene derivative with the catalyst. In fact, the reduction of benzene in the presence of 1-hexene resulted in the formation of cyclohexene in amounts 4–5 times greater than the cyclohexane conversion. The products from competitive hydrogenations of benzene and a number of olefinic systems have consistently included cyclohexene in addition to the saturated hydrocarbons.

## Experimental Section

**Reagents and Solvents.** All procedures were carried out in an argon atmosphere in a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri Train or in a conventional vacuum system. Anhydrous cobaltous chloride was purchased from Alfa Chemicals, and the trialkyl phosphites were purchased from Strem Chemicals. These reagent grade chemicals were degassed and used without further purification. Reagent grade tetrahydrofuran was refluxed 48 h over sodium hydroxide, distilled onto lithium aluminum hydride, and refluxed for 48 h before the final distillation. Reagent grade benzene and other substrates were dried by refluxing over lithium aluminum hydride or calcium hydride for 12 h before distilling. Purified hydrogen (99.95%) was purchased from Matheson & Co.

**Physical Measurements.** Proton NMR were recorded at ambient temperatures unless otherwise noted on a Varian Associates A-60A or Bruker HFX 90 spectrometer. Chemical shifts were referenced to TMS. Hydrogenation substrates and products were analyzed with a Perkin-Elmer 990 gas chromatograph with a flame ionization

detector or with a Finnegan 3300 GC/MS interfaced with a System Industries System 150. Analytical determinations were provided by Franz Pascher Laboratories, Bonn, Germany.

**Procedure for Hydrogenation Reaction.** The catalyst (0.112 mmol) was dissolved in 1 ml (11.25 mmol) of benzene in a vessel equipped with a Kontes high-vacuum stopcock. The solution was frozen at  $-196^\circ C$  and evacuated. One atmosphere of hydrogen (99.95% purity) was introduced into the system. The stopcock was closed and the reaction vessel was allowed to warm to room temperature. The solution was stirred (magnetically) for 24 h. The volatile products were vacuum-distilled and analyzed by NMR, gas chromatography, and/or mass spectrometry. In competitive hydrogenations, the same procedure was followed with an equimolar mixture of benzene and olefin. Benzene:cyclohexane and olefin:alkane ratios were determined by GC analysis with an ethyl *N,N*-dimethylxamate column.<sup>14</sup>

$\eta^3-C_3H_5Co[P(OCH_3)_3]_3$ . Synthesis procedure has been reported.<sup>11</sup> The compound was further purified by elution with pentane through neutral alumina. The alumina was slurried in a pentane/trimethyl phosphite (4:1 v/v) solution and washed with pentane prior to use.

$\eta^3-C_3H_5Co[P(OC_2H_5)_3]_3$ . Allyl iodide (0.34 ml, 4.3 mmol) was added to a slurry of  $KCo[P(OC_2H_5)_3]_4$  (4.0 g, 5.2 mmol) in 100 ml of tetrahydrofuran. The reaction was stirred at room temperature for 12 h. Solvent was then removed in vacuo, and the product was extracted from the residue with pentane. Chromatographic purification was effected with alumina pretreated with triethyl phosphite (vide supra). <sup>1</sup>H NMR:  $\delta$  -1.21 (triplet, 27) ( $J_{H-H} = 7.3$  Hz), -4.05 (multiplet, 18), -2.35 (doublet of quartets, 2) ( $J_{H_{syn}-P} = 3.0$  Hz,  $J_{H_{syn}-H} = 6.0$  Hz), -4.88 (multiplet, 1),  $\sim$ -1.3 ppm (doublet of quartets, partly obscured by phosphite resonance). Anal. Calcd: C, 42.14; H, 8.36. Found: C, 41.61; H, 8.99.

$\eta^3-C_3H_5Co[P(OCH_3)_2]_2[P(O-i-C_3H_7)_3]$ . One gram (2.0 mmol) of  $\eta^3-C_3H_5Co[P(OCH_3)_3]_3$  was stirred at room temperature in an acetonitrile solution containing 8.6 ml (40 mmol) of triisopropyl phosphite. After 10 days, the volatiles were removed under vacuum and the residue was extracted with pentane. The yellow-brown product was recrystallized from pentane at  $-40^\circ C$ . The extent of ligand substitution was determined by <sup>1</sup>H NMR. The methyl groups of  $P(OCH(CH_3)_2)_3$  were represented by a doublet,  $\delta$  -1.22 ppm ( $J_{H-H} = 6.0$  Hz). A multiplet at  $\delta$  -3.55 ppm was assigned to the methyl groups of  $P(OCH_3)_3$ . Integrated intensities of the two methyl resonances were equal, indicating a 2:1 ratio of methyl to isopropyl phosphite ligands. The allyl ligand was  $\pi$  bonded; a doublet of quartets at  $\delta$  -2.34 ppm was assigned to the *syn* protons ( $J_{H_{syn}-P} = 3.2$  Hz,  $J_{H_{syn}-H} = 5.0$  Hz). The resonance of the anti protons,  $\delta$   $\sim$ -1.22 ppm, was obscured by isopropyl phosphite peaks. A broad resonance  $\delta$  -4.86 ppm (relative intensity 4) was assigned to the unique proton of the allyl and the single protons of isopropyl phosphite.

$\eta^3-C_3H_5Co[P(O-i-C_3H_7)_3]_3$ . Four grams (5.56 mmol) of  $Co[P(O-i-C_3H_7)_3]_3Cl^{12}$  was dissolved in 100 ml of tetrahydrofuran. To this was added 5.56 mmol of freshly prepared allyllithium<sup>15</sup> in ether solution. The reaction was stirred for 4 h before the solvent was removed in vacuo. The residue was extracted with pentane and recrystallized from 10 ml of diethyl ether at  $-40^\circ C$ . The orange crystals were further purified by (1) chromatography through neutral alumina pretreated with triisopropyl phosphite and (2) a second recrystallization from ether. Anal. Calcd: C, 49.72; H, 9.39; Co, 8.15. Found: C, 49.82; H, 9.65; Co, 7.99. <sup>1</sup>H NMR:  $\delta$  -1.32 (doublet, 54) ( $J_{H-H} = 6.5$  Hz), -2.19 (doublet of quartets, 2) ( $J_{H_{syn}-P} = 4.0$  Hz,  $J_{H_{syn}-H} = 6.0$  Hz), -4.90 (multiplet, 9) ( $J_{P-H} = 8.8$  Hz,  $J_{H-H} = 6.4$  Hz),  $\sim$ -1.3 ppm (obscured by phosphite resonance).

$\eta^3-C_3H_5Co[P(CH_3)_3]_3$ .  $Co[P(CH_3)_3]_3Cl^{16}$  (2.5 g, 8 mmol) was dissolved in 50 ml of dimethoxyethane. The solution was cooled to  $-78^\circ C$  and an ether solution of freshly prepared allyllithium (8 mmol) was added dropwise. The reaction was stirred for 30 min at  $-78^\circ C$ , warmed to room temperature, and stirred for 2 h. After solvent was evaporated, the residue was extracted with hexane. The extracts were concentrated to give a deep red oil, and sublimation at  $30$ – $35^\circ C$  under high vacuum produced red-orange crystals. Melting point data: discolors,  $110^\circ C$ ; melts,  $>140^\circ C$ . Anal. Calcd: C, 43.90; H, 9.76. Found: C, 43.92; H, 9.90. <sup>1</sup>H NMR:  $\delta$  +1.01 (quintet, 2) ( $J_{H_{anti}-P} \approx J_{H_{anti}-H} \approx 7$  Hz), -1.10 (triplet,  $\sim$ 27) ( $J_{H-P} = 2.4$  Hz), -1.38 (quintet, partly obscured by phosphine protons) ( $J_{H_{syn}-P} \approx J_{H_{syn}-H} \approx 5$  Hz), -3.9 ppm (broad, 1).

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**Registry No.**  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, 42603-27-0;  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub>, 51266-17-2;  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(OCH<sub>3</sub>)<sub>2</sub>P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub>, 59830-91-0;  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, 59830-92-1;  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Co[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub>, 59830-93-2; benzene, 71-43-2; 1-hexene, 592-41-6; *n*-hexane, 110-54-3; cyclohexane, 110-82-7; cyclohexene, 110-83-8; allyl iodide, 556-56-9; KCo[P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 51371-42-7; Co[P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>]<sub>3</sub>Cl, 59830-94-3; allyllithium, 3052-45-7; Co[P(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>Cl, 55516-89-7.

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## Photoinduced Oxidation of Coordinated Ligands in *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Generation of a Decarbonylation Agent

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Ultraviolet irradiation of air-saturated solutions of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] results in oxidation of CO to CO<sub>2</sub> and PPh<sub>3</sub> to Ph<sub>3</sub>PO and formation of an oligomeric complex formulated as [RhCl(O<sub>2</sub>)(Ph<sub>3</sub>PO)<sub>0.67</sub>]<sub>x</sub>. The 254 and 366 nm disappearance quantum yields for *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] are 0.02, and quantum yields of other *trans*-[RhCl(CO)L<sub>2</sub>] (L = PMePh<sub>2</sub>, PMe<sub>2</sub>Ph, PEtPh<sub>2</sub>, PEt<sub>2</sub>Ph, PEt<sub>3</sub>) complexes vary from 0.01 to 0.05. The rhodium containing photoproduct from the photolysis of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] can be converted into [RhCl(PPh<sub>3</sub>)<sub>3</sub>] by treatment with excess PPh<sub>3</sub> in refluxing ethanol, and the photoproduct with excess PPh<sub>3</sub> will decarbonylate benzaldehyde and phenylacetyl chloride to give *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>], benzene, and benzyl chloride, respectively.

## Introduction

It is now well-established<sup>1-3</sup> that [RhCl(PPh<sub>3</sub>)<sub>3</sub>] is a useful reagent for affecting the decarbonylation of aldehydes and acyl and aroyl halides, presumably by acting through three-coordinate [RhCl(PPh<sub>3</sub>)<sub>2</sub>] (eq 1-2).<sup>4</sup> The reactions are stoichiometric with 1 mol of rhodium complex required for each mole of carbonyl compound consumed. The reactions cannot be made catalytic at a useful temperature because *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] does not lose carbon monoxide and the active reagent cannot be regenerated thermally.<sup>5,6</sup> Since a large number of transition metal carbonyl complexes are known to dissociate CO upon irradiation,<sup>7</sup> it was our initial expectation that [RhCl(PPh<sub>3</sub>)<sub>2</sub>] or its dimer could be formed from *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] through photoinduced loss of carbon monoxide. The decarbonylation cycle would then be complete and the reaction could be made catalytic by continuous photolysis. We have examined the photochemical properties of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] and have observed, however, that simple photoelimination of CO does not occur, but rather that CO and PPh<sub>3</sub> are oxidized to CO<sub>2</sub> and Ph<sub>3</sub>PO upon irradiation of the complex in the presence of oxygen. The details of this photochemical study are reported herein, and methods are presented for the easy and convenient conversion of the rhodium containing photoproduct into [RhCl(PPh<sub>3</sub>)<sub>3</sub>] and for recycling rhodium in the decarbonylation scheme.

## Experimental Section

Triethylphosphine and triphenylphosphine were obtained from the Aldrich Chemical Co., and PPh<sub>3</sub> was recrystallized from EtOH before use. PMePh<sub>2</sub>, PMe<sub>2</sub>Ph, PEtPh<sub>2</sub>, and PEt<sub>2</sub>Ph were synthesized from

PPh<sub>2</sub>Cl and PPhCl<sub>2</sub> and the appropriate Grignard reagent following an adaptation of the published procedure.<sup>8</sup> The *trans*-[RhCl(CO)L<sub>2</sub>] complexes were prepared according to the literature.<sup>9-11</sup>

**Irradiation Procedures.** The irradiations were conducted using either a low-pressure Hg arc lamp (254 nm) or a 450-W Hanovia medium-pressure Hg arc lamp equipped with Corning 0-52 and 7-37 glass filters (366 nm). The disappearance quantum yields were measured at 254 and 366 nm using ferrioxalate actinometry and a conventional merry-go-round apparatus by following the decrease in intensity of the principal absorption band near 365 nm of oxygen-saturated CH<sub>2</sub>Cl<sub>2</sub> solutions of each of the complexes. Photolyses were conducted in standard 1.0 cm path length quartz uv spectrophotometer cuvettes, in 1.0 mm NaCl infrared solution cells, or in 300 ml Pyrex flasks for isolation of the photoproducts. Uv-visible and infrared spectral changes occurring during the photolyses were obtained for all the *trans*-[RhCl(CO)L<sub>2</sub>] complexes and were virtually identical. Measurement of the stoichiometry of the reaction and characterization of the photoproduct were only performed for *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>], detailed below.

**Photolysis of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>].** Irradiation of oxygen-saturated toluene or CH<sub>2</sub>Cl<sub>2</sub> solutions of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] induces a rapid color change from yellow to orange-red. Irradiated toluene solutions deposit a tan precipitate which after washing with EtOH and Et<sub>2</sub>O analyzes approximately for [RhCl(O<sub>2</sub>)(Ph<sub>3</sub>PO)<sub>0.67</sub>]<sub>x</sub>. Calcd: C, 40.47; H, 2.81; Rh, 28.92; Cl, 9.96; P, 5.84; O, by difference, 12.01. Found: C, 37.23; H, 3.24; Rh, 28.52; Cl, 9.91; P, 5.47; O, by difference, 15.63. A solution of 0.5054 g (0.73 mmol) of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] irradiated to completion in toluene yielded 0.2549 g (0.92 mmol) of uncoordinated Ph<sub>3</sub>PO isolated by evaporation of the irradiated solution followed by repeated washing of the resultant tan solid with EtOH and finally sublimation of Ph<sub>3</sub>PO. Oxygen uptake measurements were performed by irradiating 20-25 ml of 6.24 × 10<sup>-3</sup> M and 1.06 × 10<sup>-2</sup> M CH<sub>2</sub>Cl<sub>2</sub> solutions of *trans*-[RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>], and the amount of O<sub>2</sub> absorbed was measured with a 10 ml micro gas buret. The entire system was maintained at a constant temperature of 23 °C, and values of 1.70, 1.60, and 1.48 mol of oxygen ab-