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Reduction of Terminal Alkynes Mediated by Tris(2,2′-bipyridine)cobalt(I)

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In buffered aqueous ethanolic solution, phenylacetylene is reduced to styrene by $[Co(bpy)_3]^+$ (bpy = 2,2′-bipyridine). In solutions of lower proton availability the predominant products were oligomeric, including coupled species such as 1,4-diphenylbutenyne.

Introduction

The tris(2,2′-bipyridine)cobalt(I) cation, $[Co(bpy)_3]^+$ (**I**), has previously been reported to mediate in the reduction of water (to dihydrogen),[1] carbon dioxide (to carbon monoxide),[2] and allyl chloride (to 1,5-hexadiene).[3] Stoichiometric and kinetics studies suggested that in aqueous solution the first two reactions involve a common intermediate,[1,2] which was considered to be a reactive cobalt–hydride species. A further interest of these studies was the fact that $[Co(bpy)_3]^+$ may be generated photochemically from the reduction of the corresponding cobalt(II) and cobalt(III) species,[4] so that the $[Co(bpy)_3]^{n+}$ moiety may act as a homogeneous catalyst in schemes for the photochemical reduction of water[1,5] and carbon dioxide,[2] using $[Ru(bpy)_3]^{2+}$ as a photosensitizer.

In the case of allyl chloride,[3] initial π-coordination of the substrate to the cobalt center was proposed, as in the case of similar substrates such as acrylonitrile and allyl alcohol, with the greater reactivity of allyl chloride allowing subsequent reaction to occur.

Satyanarayana and Periasamy[6] reported the reaction of $CoCl_2$, $NaBH_4$, and PPh_3 with terminal alkynes to produce *trans,trans*-1,3-dienes. The authors suggested the insertion of an alkyne into the cobalt–hydride bond of a species formed *in situ* by reduction of a (triphenylphosphine)cobalt(II) complex by BH_4^- as an initial step in the reaction. However, recent studies by Bianchini *et al.*[7] have shown that the reaction of 16-electron $[Co(PP_3)]^+$ $\{PP = P(CH_2CH_2PPh_2)_3\}$ fragments with terminal alkynes initially resulted in the π-alkyne species (as a kinetic product), which in turn isomerized to the hydride–alkynyl and ultimately to the vinylidene species, which is considered the thermodynamically stable product.

The dichotomy between the potential of $[Co(bpy)_3]^+$ as a general hydrogenation catalyst for unsaturated organic substrates and the rich chemistry of cobalt(I) centers with alkynes, prompted us to attempt a preliminary stoichiometric and kinetic study of the course of the reactions of $[Co(bpy)_3]^+$ with terminal alkynes. The results of this study are now reported.

Experimental Section

General Comments. Product determinations of H_2 were obtained by GC (molecular sieve 5A support; 35 °C; argon carrier gas; thermal conductivity detector (50 °C); injector temperature, 75 °C). Separation and purification of organic products were performed by HPLC (Si-100 7-μm column; low-boiling petroleum ether eluent), and by column chromatography under reduced pressure (silica gel adsorbent; petroleum ether or petroleum ether/ethyl acetate mixtures as eluents).[8]

Ethanol, diethyl ether, benzene, ethyl formate, and low-boiling petroleum ether were purified by the respective literature methods.[9,10] Alkyne reagents were checked for purity by ^{1}H-NMR (300-MHz) techniques and, except for phenylacetylene, required no further purification. Phenylacetylene had a 2% styrene impurity and was freshly purified by vacuum distillation as required.

All other reagents were used without further purification.

Sodium amalgam (0.9%) was prepared by the method established in the literature.[9] Solid $[Co(bpy)_3]Cl$ was prepared and recrystallized using the literature method (overall yield 80%).[2,11]

$[Co(bpy)_3]^+$ is extremely air sensitive, and consequently, all manipulations involving this reagent were performed in a Vacuum Atmospheres HE-Series glovebox under an argon atmosphere.

Buffer Solutions. Buffer solutions were obtained by addition of appropriate quantities of NaOH to aqueous solutions of acetic, chloroacetic, or formic acid. For acid catalysis studies, [base$^-$] was maintained at 0.2 mol dm^{-3}, and the acid concentration was varied to attain the same pH (3.7) for each buffer. For all other studies an acetate buffer was used, with [HOAc] = [OAc$^-$] = 0.2 mol dm^{-3}: reaction mixtures requiring buffer contained 10% v/v of this aqueous buffer solution, unless otherwise stated.

Stoichiometry Studies. In a typical reaction, appropriate quantities of buffer (or water), ethanol, and alkyne were added to a 60-mL glass vessel, followed by addition of a 0.041 mol dm^{-3} ethanolic solution of $[Co(bpy)_3]^+$, and the vessel was sealed with a septum cap. For most reactions 2.5 mL of the cobalt solution was used to make up a total volume of 10 mL. The stoppered vessels were left until the reaction was complete, as indicated by the loss of the blue color of Co(I), or the lack of further color change after several days. The reaction mixture was acidified (1 mol dm^{-3} HCl), the organic products were extracted into low-boiling petroleum ether (3 × 10 mL) and washed with a saturated aqueous solution of NaCl, and the solvent was removed on the rotary evaporator. ^{1}H and ^{13}C NMR spectra (300 and 75 MHz,

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respectively) were obtained in $CDCl_3$ using dinitrobenzene, where appropriate, as an internal standard.

The concentrations of $[Co(bpy)_3]^+$ stock solutions for all studies were determined spectrophotometrically (absorption coefficient ϵ_{605} = 6500 $m^2\ mol^{-1}$).[12]

Where an estimate of the yield of H_2 was required, a sample of the gas (0.25 or 1.0 mL as appropriate) above the solution was taken: the overall gas volume above the liquid was evaluated in each sample by water displacement.

Kinetic Studies. Reaction mixtures for the following *in situ* analyses were prepared as described above, utilizing smaller reaction vessels (total volume = 13 mL), and the reaction mixture volume was varied from 1 to 5 mL as appropriate. Reaction mixtures for kinetic studies involving acid catalysis were prepared by the addition of a solution of $[Co(bpy)_3]^+$ (0.2 mL, 0.041 mol dm^{-3}) to an ethanol (4.29 mL) solution containing buffer (0.5 mL) and phenylacetylene in a 5-fold excess (0.01 mL). After preparation, the mixtures were immediately transferred to gastight 2-mm cuvettes fitted with ground glass stoppers, and the decay of $[Co(bpy)_3]^+$ was measured spectrophotometrically (at 605 nm). Infinity readings were obtained after exposing the solutions to air.

Results

The addition of the terminal alkynes phenylacetylene or 1-decyne in excess to acetate-buffered aqueous ethanol solutions containing $[Co(bpy)_3]^+$ leads to an increased rate of consumption of the blue reductant, compared with the rate in the absence of the alkyne.

The organic products of such reactions were analyzed for various alkynes and compared with the reaction products in nonbuffered aqueous ethanol solutions. The analysis of dihydrogen was performed for the reactions of phenylacetylene in buffered aqueous ethanol solutions of $[Co(bpy)_3]^+$ to investigate the extent of the competition between this substrate and water for the proposed cobalt–hydride intermediate.

Stoichiometry Studies. The reactions of phenylacetylene with $[Co(bpy)_3]^+$ were studied in aqueous ethanol solutions in which the water content was varied from 0.5 to 10%. The majority of the organic products were unidentified aromatic compounds, presumably oligomeric species. Diphenylbutadiyne and *cis/trans*-1,4-diphenylbutenyne were detected in the reaction mixtures with a water content up to 5%. The greatest yield of *cis/trans*-1,4-diphenylbutenyne was 18% (based on eq 1), obtained in mixtures containing 1% water, whereas diphenylbutadiyne was present only in trace quantities.

$$[Co(bpy)_3]^+ + 3PhC{\equiv}CH \rightarrow PhC{\equiv}C{-}CH{=}CHPh + [CoH(bpy)_2(C{\equiv}CPh)]^+ \quad (1)$$

For a series of equivalent reactions conducted in aqueous ethanol with acetate buffer, the dominant feature was the hydrogenation of phenylacetylene to styrene. The greatest yield was observed for the 90% ethanol solution and was evaluated to be 44% on the basis of the reaction given in eq 2. At a lower water content the styrene yield diminished,

$$2[Co(bpy)_3]^+ + PhC{\equiv}CH + 2H^+ \rightarrow PhCH{=}CH_2 + 2[Co(bpy)_3]^{2+} \quad (2)$$

and no styrene was detected in solutions with an H_2O content below 5%. 1,4-Diphenylbutenyne was detected in reaction mixtures with low water content, although the yields were much less than observed in the absence of buffer (see above). Unidentified aromatic oligomers were also present in these samples, and the proportion of oligomers increased with lower water content.

Table 1. H_2 Yields for the Reaction of Phenylacetylene and $[Co(bpy)_3]^+$ in Buffered 90% Ethanol Solutions (Total Volume of Reaction Mixtures = 10 mL)

$[PhC{\equiv}CH]/mol\ dm^{-3}$	$[Co(bpy)_3^+]/mol\ dm^{-3}$	H_2/mL
0.039	0.038	0.02
0.039	0.076	0.04
0.156	0.038	0.01
0	0.038	2.44

The reaction was examined with a number of other alkyne substrates. Addition of $[Co(bpy)_3]^+$ to separate buffered 90% ethanol solutions of 4-octyne and diphenylacetylene generated no organic products. Indeed, diphenylacetylene and 4-octyne apparently inhibited the reaction of $[Co(bpy)_3]^+$ with water, as indicated by the length of time required for the oxidation of Co(I). Reaction of 1-decyne and $[Co(bpy)_3]^+$ under the same conditions produced some hydrogenated product, although the yield was very low, suggesting that the hydrogenation reaction requires suitably activated monosubstituted alkynes.

The reactions were also analyzed to determine the effect of the presence of the alkynes on reduction of water by $[Co(bpy)_3]^+$. The addition of this reductant to similar solutions of aqueous ethanol (with and without acetate buffer) in the absence of phenylacetylene results in the reduction of water to dihydrogen (H_2). The significant finding from the present work was that the presence of phenylacetylene almost completely inhibits the reduction of water to H_2. As an example, the H_2 yields from the reaction of phenylacetylene and $[Co(bpy)_3]^+$ in buffered 90% ethanol are presented in Table 1. For samples which are equimolar in phenylacetylene and $[Co(bpy)_3]^+$, the production of H_2 was reduced by 2 orders of magnitude compared with that observed in the absence of the alkyne. Additional experiments of this type showed that increasing the water content of the buffered solution to 40% had very little effect on the inhibition of H_2 production by phenylacetylene.

Spectral Observations. The addition of phenylacetylene to a solution containing $[Co(bpy)_3]^+$ significantly modifies its electronic spectral characteristics over the region 350–650 nm. It is apparent that there is interaction between phenylacetylene and $[Co(bpy)_3]^+$.

An attempt was made to identify the nature of the interaction using IR methods. In previous studies, π-alkyne, σ-alkynyl, and vinylidene attachment to cobalt by alkynes has been reported.[7,13] In the present instance, using *in situ* studies, no bands were detected that could be assigned to linkages of π-alkyne, σ-alkynyl, or hydride to the metal center. The vinylidene and σ-alkenyl structures, although not evident, cannot be discounted, as their IR absorptions may be obscured by absorptions due to the polypyridyl ligands. It should also be noted that the nonobservance of absorptions in the region 2200–1900 cm^{-1} may not eliminate a σ-alkynyl compound, since

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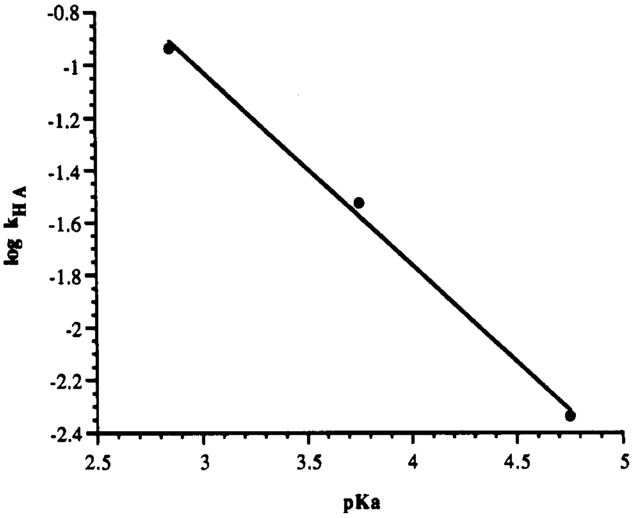


Figure 1. Plot of log k_{HA} vs buffer pK_a for the oxidation of Co(I) in buffered 90% ethanol solutions containing $[Co(bpy)_3]^+$ (1.6×10^{-3} mol dm^{-3}), phenyacetylene (18×10^{-3} mol dm^{-3}), and 10% v/v aqueous buffer. For aqueous buffer solutions: [base] = 0.2 mol dm^{-3}; pH = 3.7; total bufffer concentrations ([HA] + [A$^-$]) were 0.225 mol dm^{-3} chloroacetate, 0.4 mol dm^{-3} formate, 2.2 mol dm^{-3} acetate.

very weak $\nu_{C\equiv C}$ absorptions have been reported in compounds of phenylacetylide attached to ruthenium[14] and iron.[15]

Similarly, *in situ* NMR studies provided no information on the interaction of phenylacetylene and the metal center, primarily because of the paramagnetic nature of the metal ion, but they provided evidence for free 2,2′-bipyridine (presumably by loss from the cobalt center) in the early stages of the reaction.

Kinetics Studies. In buffered aqueous ethanol solutions, the reaction of phenylacetylene and $[Co(bpy)_3]^+$ is first order with respect to the concentration of the complex ion, and for equimolar mixtures of phenylacetylene and $[Co(bpy)_3]^+$ the rate of loss of cobalt(I) is comparable to that found for similar solutions without the alkyne present. The latter reaction produces dihydrogen from the reduction of water, while the former results in the hydrogenation of phenylacetylene to styrene. The similarity in rates for these two processes indicates that the inhibition of dihydrogen production by phenylacetylene is not due to a kinetic factor in the competition between phenylacetylene and water for the intermediate $[CoH(bpy)_2(H_2O)]^{2+}$; the similarity in rate appears to be coincidental, rather than the function of a common step in the mechanism. The initial attachment of the alkyne to the metal center is consistent with these results.

The involvement of buffer in the hydrogenation of phenylacetylene is evident from the reaction rate studies, and there is a requirement of buffer for the formation of hydrogenation products. Reaction mixtures without added buffer often remained blue for several days, compared with a half-life of minutes in the case of the buffered solutions.

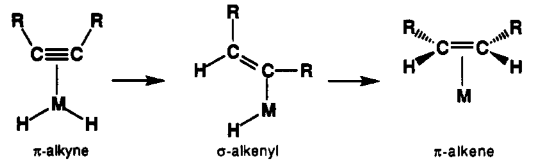
The rate of loss of cobalt(I) was found to be strongly inhibited by added bpy, indicating loss of one (or more) of these ligands from the metal center prior to the rate-determining step.

For the current study, the effect of acetate, formate, and chloroacetate buffers was investigated with a view to elucidating the nature of the involvement of the buffer. A Brønsted plot[16] of $k_{HA} = k(\mathrm{obs})/[HA]$ vs buffer pK_a (Figure 1) for the reaction of phenylacetylene and $[Co(bpy)_3]^+$ in 90% ethanol/10% buffer indicates this reaction is general-acid catalyzed. The large value of α (0.73) obtained gives a strong indication of acid catalysis, suggesting proton donation is an important feature of the hydrogenation reaction.

Discussion

The results obtained in this study suggest that the initial reaction between $[Co(bpy)_3]^+$ (**I**) and alkynes is the attachment of the substrate to the metal center. The formation of a π-alkyne organometallic compound from the interaction of alkynes with transition metals is well established in the literature, and the mechanisms discussed below are based on this assumption.

Hydrogenation Mechanisms. Alkyne hydrogenations reported in the literature almost invariably proceed via a pathway involving a σ-alkenyl species.[15,17-22]



Such a mechanism requires the presence of a hydride moiety adjacent to the alkyne, with subsequent insertion of the organic species into the M–H bond. For the present system, a hydride is not generated prior to attachment of an alkyne to the cobalt center. The π-alkyne formed initially (**II**; Scheme 1) possibly rearranges to the vinylidene species,[7] and reaction with a proton source would produce the σ-alkenyl (**III**) by either ligand protonation[23,24] or metal–hydride formation and subsequent insertion of the alkyne into the Co–H bond.

Further reaction with a proton source and insertion can account for the production of styrene and complete oxidation of cobalt(I). An alternative reaction of the σ-alkenyl species, involving reaction of additional alkyne, is well documented in the literature:[14,15,25] this mechanism requires the oxidative addition of phenylacetylene and reductive elimination of styrene and results in the formation of a σ-alkynyl species (**IV**) which may then react with further alkyne to produce enynes, diynes, and higher

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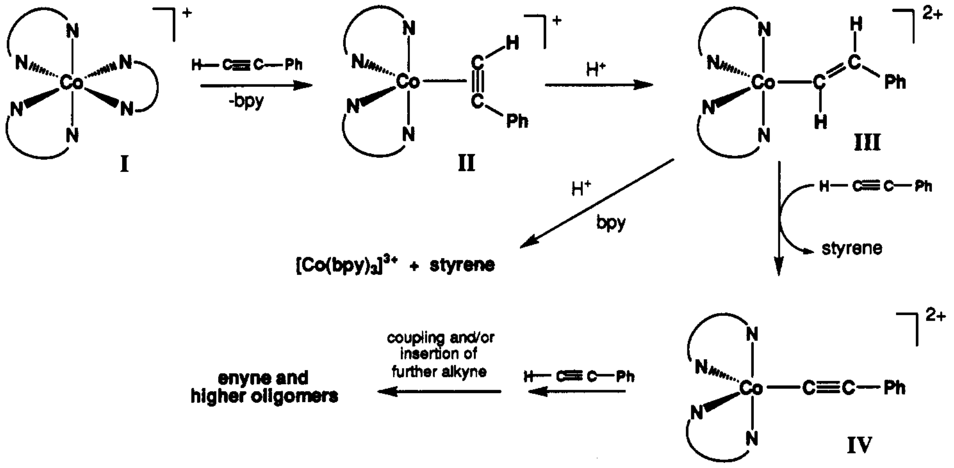
Scheme 1. Proposed Pathway for the Reactivity of $[Co(bpy)_3]^+$ with Phenylacetylene in Buffered Aqueous Ethanolic Solution



oligomers. This is consistent with the observation of these products in buffered ethanol solutions of low water content.

The conclusion that may be drawn is that there are competing reactions for the σ-alkenyl species, dependent on proton availability. In solutions of high water content, the predominant product is styrene. As the water content and proton availability is reduced, the reaction with additional phenylacetylene is favored. Although no intermediates were detected in this study, this mechanistic scheme accounts for the kinetics data and the absence of hydrogenation products at low water content (because the initial step after attachment of phenylacetylene requires reaction with a proton source) and is consistent with the literature precedents.

Oligomerization Mechanisms. Reaction of phenylacetylene with $[Co(bpy)_3]^+$ in the absence of buffers produced 1,4-diphenylbutenyne as well as oligomeric compounds. The dimerization of 1-alkynes to enynes, mediated by transition metal complexes, usually occurs through the reaction of a σ-alkynyl compound with additional alkyne.[14,25,26] In the current system, this may be rationalized by initial oxidative addition of phenylacetylene to the cobalt center (with loss of one bpy ligand) to form a σ-alkynyl/hydride compound which in turn reacts with additional phenylacetylene to produce a species containing one σ-alkynyl and one π-alkyne linkage; coupling or insertion between these two groups would produce an enynyl compound. Higher oligomers may be generated by further reactions of this type. Alternatively, and more likely according to several authors,[14,26,27] the π-alkyne rearranges to the vinylidene derivative and formation to the enynyl compound occurs through coupling of the vinylidene and σ-alkynyl moieties.[28] Both these alternatives have no proton requirement and are consistent with the greatest yield of enyne being observed in reaction mixtures with low proton availability.

Conclusion

It has been established that the cobalt hydride intermediate implicated in the reduction of water and CO_2 is not involved in the hydrogenation of alkynes. The feasibility of the mediation of alkyne reductions by $[Co(bpy)_3]^+$ was investigated, and although many complications in these reductions were apparent, the selective hydrogenation of phenylacetylene was observed under conditions of ready proton availability.

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