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THE REACTION OF ALKYL-1-YNES WITH Rh^I, Co^I AND Co^{III} DERIVATIVES OF *N,N'*-ETHYLENEBIS(SALICYLALDIMINE)(SALENH$_2$)

A.M. VAN DEN BERGEN, R.L. ELLIOTT, C.J. LYONS, K.P. MACKINNON and B.O. WEST*
Chemistry Department, Monash University, Clayton, Victoria, 3168 (Australia)

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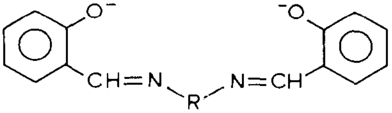
Summary

Electrochemical or chemical reduction of $[Rh(Salen)py_2]PF_6$ in THF produces a mixture of Rh^I species which can react with phenylethyne to produce the σ-bonded ethynyl derivative $C_6H_5C_2Rh(Salen)py$. $[Co^I(Salen)]^-$ does not react readily with phenylethyne but does with 3,3,3-trifluoroprop-1-yne to yield $CF_3C_2Co(Salen)py$ in 80% yield. High yields of $C_6H_5C_2Co(Salen)py$ can be obtained when $C_6H_5C_2H$ reacts with $[Co(Salen)]_2O_2$ (79% yield) or Co(Salen)(acac) (ca. 100% yield) in pyridine/dimethylsulfoxide mixtures at 120°C. Hex-1-yne does not react with $[Co^I(Salen)]^-$ or the peroxy-Co^{III} complex.

Introduction

Despite the wide range of metal alkynyl derivatives that have been synthesized [1], little attention has been paid to compounds having σ-bonded alkynyl groups bound to metals coordinated in turn by acid-base chelate ligands. Several Co^{III} derivatives have been reported. Thus $C_6H_5C_2Co(Dmg)_2py$ (Dmg = anion of dimethylglyoxime) has been prepared [2] by a Grignard reaction upon $ClCo(Dmg)_2py$ or the oxidative reaction of $C_6H_5C_2Br$ on $[Co(Dmg)_2]^-$ [3] while RCo(SB) complexes ($R = C_6H_5C_2$; p-$CH_3C_6H_4C_2$: SB = Salen, Sal-1,2-pn (Scheme 1)) have been prepared [4] by direct reaction of the corresponding ethynes on Co^{III} species of an indefinite nature prepared by passing oxygen through a solution of the Co^{II} complexes in methanol. This method was suggested by the authors to be of potentially wide application. A number of transition metal phthalocyanine complexes also add alkynyl groups when Li-phenylethynyl reacts with $M^{II}(Pc)$ complexes to give $Li_2[M(Pc)R_2]$ species [5].



SCHEME 1. Abbreviations of ligands. ($R = (CH_2)_2$ (Salen); $CH(CH_3)CH_2$ (Sal-1,2-pn); $(CH_2)_3$ (Sal-1,3-pn))

Rh^{III}-σ-bonded alkynyl complexes have been formed by the oxidative-addition reaction of alk-1-ynes with Rh^I complexes having π-acid ligands bound to Rh [6], and this raises the possibility that Rh^I complexes with acid-base chelate groups attached, such as $[Rh^I(Salen)]^-$, might also undergo oxidation-addition with alk-1-ynes. Rh^{III} organometallics R-Rh(Salen)py have been found to form [7,8] when alkyl halides react with the Rh^I species.

The reaction of a variety of alkynes with $[Co^I(Dmg)_2]^-$ has, however, yielded vinylidene or other alkenyl derivatives $(R_1)(H)C{=}C(R_2)Co(Dmg)_2$, not alkynyl [3]. The formation of the Co^I complex in these reactions was by $[BH_4]^-$ reduction of the Co^{II} complex in aqueous methanolic solution whether in the presence of alkali or weak acid and the reactions have been considered to involve addition of the alkyne to a Co–H bond thus producing the alkenyl products. The direct reaction of alkynes with a "simple" $[Co^I(Chel)]^-$ complex in the absence of reagents which could form H–Co(Chel) has not previously been reported.

This paper reports some studies to determine whether α-alkynyl derivatives can be formed by reaction of several alk-1-ynes with Rh^I and Co^I(Salen) complexes as well as some further experiments related to the "McKenzie" route [4] for preparing Co^{III}-alkynyl derivatives.

Results

The formation of $[Rh^I(Salen)]^-$ species

Previous accounts have been given of the successful preparation of alkyl-Rh^{III}(SB) derivatives (SB = Salen, Sal-1,3-pn, Salphen) by reaction of alkyl halides with the products formed when Rh^{III}(Salen)pyCl [7] or *trans*-$[Rh^{III}\text{-}(Salen)py_2]PF_6$ [8] are reduced with sodium amalgam. Because of some redox reactions observed between the reduced Rh species and the Rh^{III} starting material, there was some uncertainty as to whether the oxidation state of Rh in the reduced solutions was to be viewed as Rh^0 [7] or Rh^I [8], the latter state being the more chemically appropriate, however for the oxidation addition reactions with alkyl halides. An electrochemical study has been carried out in an attempt to define the oxidation state of the product formed on reduction of $[Rh^{III}(Salen)py_2]PF_6$.

In tetrahydrofuran solution (0.5 *M* $NaClO_4$) D.C. polarographic reduction of the Rh^{III} complex results in a single large wave being observed, reduction commencing at ca. −0.75 V and being complete at ca. −1.25 V (vs. a standard calomel electrode). The plot of E vs. $\log(i/i_d - i)$ for this wave is not linear and may be viewed as a composite of two straight lines with slightly differing slopes, (slope = 65 for the 'best fit' line in the voltage range (−0.75 to −0.95 V), $E_{1/2} = -0.912$ V; slope = 54.5 for the 'best fit' line in the range −0.95 to −1.25 V, $E_{1/2}$ −0.915 V; the overall 'best fit' line has slope = 54, $E_{1/2}$ −0.915 V). The slopes for the component lines are each greater than required for a 2 electron reduction as is also the overall slope for the 'best fit' line. The values, however, differ somewhat from the slopes expected for single electron processes although being relatively close to the theoretical slope of 59. Constant potential coulometry carried out on a sample of $[Rh(Salen)py_2]PF_6$ at −1.30 V in the presence of 5% of pyridine gave $n = 2$ indicating that 2 electron equivalents are required for reduction of the complex although no clearly defined single electron steps can be observed. The formal oxidation state of the Rh in the reduced complex is thus Rh^I. During the reduction process free pyridine could be

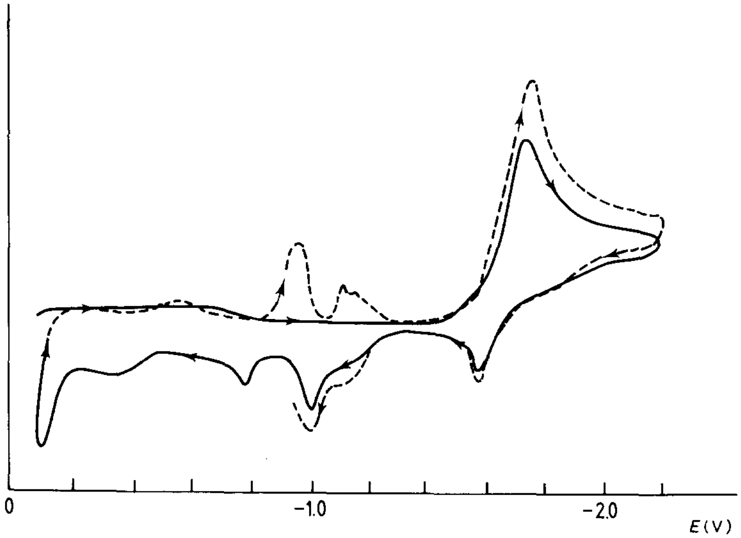


Fig. 1. Cyclic voltammogram of $[Rh(Salen)py_2]PF_6$ (0.5×10^{-3} *M*, tetrahydrofuran, 0.5 *M* $[(C_4H_9)_4N][ClO_4]$, Hg drop, scan rate 1 V/s^{-1}); ——— first cathodic and anodic sweeps. ------ second sweep.

detected polarographically and essentially two moles of pyridine have been released when reduction is complete, suggesting the constitution of the Rh^I complex as the four-coordinate complex $[Rh^I(Salen)]^-$. The initial orange colour of the Rh^{III} complex changes to red-brown on complete reduction although a transient green stage is observed in the early stages if reduction is carried out slowly. Cyclic voltammograms obtained on slowly growing mercury drops [9], however, have demonstrated that several Rh^I products are obtained on reduction which can reoxidise to new, higher valent Rh species (Fig. 1). The cyclic voltammograms, however, were severely effected by absorption phenomena at voltages close to the reduction potential of the initial Rh^{III} derivative and proved only of limited use in examining the behaviour of the solutions. Platinum was even more liable to such absorption problems and could not be used successfully for CV studies.

Polarographic examination also indicated the presence of three major species in the fully reduced Rh^I solutions, a component reoxidising at −0.84 V comprising 20%, the major component reoxidising at −0.58 V comprising 60% and a further wave at −0.03 V comprising 19% of the total Rh content.

Addition of CH_3I to such a "Rh^I(Salen)" system nevertheless resulted in the alkyl Rh complex $CH_3Rh(Salen)py$ being isolated in good yield (ca. 70%) indicating that whatever their individual constitutions, the complexes undergo similar oxidative-addition reactions with organic halides.

Chemical reduction of $[Rh^{III}(Salen)py_2]PF_6$ in THF using sodium amalgam produced a similarly coloured brown-red solution to that produced electrochemically and the reduced solution was found to contain a similar range of Rh^I products by polarographic and cyclic voltammetric examination to that observed on electrochemical reduction. There is thus no doubt that similar Rh^I compounds are formed by chemical or electrochemical reduction of [Rh^{III}(Salen)py$_2$]PF$_6$ although the exact nature of these species is yet to be fully defined.

A coulometric study of the reoxidation of the Rh^{I} species formed by the 2 electron reduction of [Rh^{III}(Salen)py$_2$]$^+$ indicates in sharp contrast that only 1 electron equivalent is required for the reverse stage, suggesting that some form of Rh^{II} complex is obtained as an electrochemically stable entity. The green-brown solution formed, however, is very sensitive to oxygen and reacts to finally yield an orange, air stable solution.

It may be noted that Calmotti and Pasini [10] have recently reported the preparation of Rh^{II}(Salen) and several other related complexes by reaction between the ligand and [Rh^{I}(CO)$_2$Cl]$_2$. ESR studies support the view that Rh^{II}(Salen) can exist as an Rh–Rh bonded dimer in pyridine solution but can dissociate in methanol. The complex was observed to absorb oxygen at room temperature.

The formation of such dimeric, metal–metal-bonded species during the reduction of [Rh^{III}(Salen)py$_2$]$^+$ can qualitatively account for the variety of final Rh species observed in the present work since a number of reduction processes, occurring at different rates, can be envisaged. Thus several of the following processes may be postulated in addition to or instead of the two-electron process Rh^{III} → Rh^{I}:

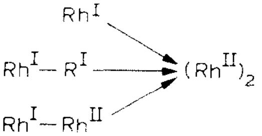
$$\mathrm{Rh^{III}} \xrightarrow{+1e} \mathrm{Rh^{II}}$$

$$\mathrm{Rh^{II}} \xrightarrow{+1e} \mathrm{Rh^{I}}$$

$$2\mathrm{Rh^{II}} \rightleftarrows (\mathrm{Rh^{II}})_2$$

$$(\mathrm{Rh^{II}})_2 \xrightarrow{+1e} \mathrm{Rh^{I}\text{–}Rh^{II}} \xrightarrow{+1e} \mathrm{Rh^{I}\text{–}Rh^{I}}$$

On reoxidation, formation of the stable dimer species could be favoured, thus accounting for the apparent restriction to a one-electron stage for all the Rh in the sample.



Further work is in progress to define which of these various stages are significant in the redox behaviour of [Rh^{III}(Salen)py$_2$]PF$_6$.

Reactions of [Rh^{I}(Salen)] and [Co^{I}(Salen)] species with alk-1-ynes

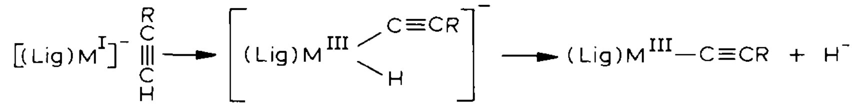
A solution of [Rh^{I}(Salen)] species in THF produced either electrochemically or by reduction with sodium amalgam does not absorb hydrogen or acetylene at atmospheric pressure. However, the complexes do react with phenylethyne and the colour of the solution changes from brown-red to orange over several hours. Thin layer chromatographic examination of the solution only disclosed the existence of a single complex which, on isolation, showed a strong infra-red spectral band at 2070 cm^{-1} indicative of a C≡C unit. The ^{1}H NMR spectrum of the complex showed resonances at 8.42 (CH : N) and 3.7 ppm (the bridging methylene groups) due to the Schiff-base ligand, at 8.22 and 7.85 ppm for the α- and γ-protons of pyridine, with a multiplet between 6.40 and 7.5 ppm accounting by integration for the β-pyridine protons, the Schiff-base aromatic protons and the phenyl ring protons of the alkynyl group. No additional protons could be detected. Microanalysis confirmed the formula of the complex to be $C_6H_5C{\equiv}CRh(Salen)py$.

Rapid reaction occurred when 3,3,3-trifluoroprop-1-yne was added to a Rh^I(Salen) solution, but a Rh^{III} complex could not be isolated successfully. A dark tarry residue separated from the reaction mixture containing C–F bonds and indicated that possibly some oligomerization of the alkyne had occurred. There was no observable reaction in the presence of hex-1-yne.

The $[Co^I(Salen)]^-$ anion is a well characterized species [11] and is readily prepared by electrochemical [9] or chemical reduction of Co^{II}-(Salen) [12]. Tetrahydrofuran solutions of the Co^I complex prepared by electrochemical reduction under scrupulously anhydrous and anaerobic conditions did not show evidence for reaction with hydrogen, acetylene or hex-1-yne even with reaction times up to 48 h at room temperature. A very slow reaction was observed with phenylethyne and a small ($< 5\%$) yield of the alkynyl $C_6H_5C{\equiv}CCo^{III}(Salen)py$ recovered. This compound was first characterized by McKenzie et al. [4] following a different synthetic route. The remaining Co^I complex in this reaction has largely been oxidised to higher valent Co compounds. The reaction mixture subjected to thin layer chromatographic examination showed a multitude (> 5) of cobalt-containing species including Co^{II}(Salen).

Immediate reaction, however, takes place between $[Co^I(Salen)]^-$ and 3,3,3-trifluoroprop-1-yne and in this case a high yield (80%) of $CF_3C{\equiv}CCo(Salen)py$ was obtained.

The most plausible mechanism for the reactions of the Rh^I and Co^I complexes would appear to involve the initial coordination of the alkyne to the metal followed by separation to σ-bonded alkynyl and hydride fragments as is found in such reactions with many Rh^I and Ir^I π-acid complexes [6].



$$[(Lig)M^I]^- \; \mathrm{HC{\equiv}CR} \longrightarrow \left[(Lig)M^{III}\begin{matrix} \diagup C{\equiv}CR \\ \diagdown H \end{matrix}\right]^- \longrightarrow (Lig)M^{III}{-}C{\equiv}CR + H^-$$

Preferential loss of the H^- ion must then have occurred in the cases where the yields of alkynyl derivative obtained were high and would be aided by strengthening of the metal–C bond by d_π–π^* interactions with the $C{\equiv}C$ system. The nature of the reaction mixtures, however, precluded a realistic search for the presence of free H^- ions.

The greater degree of reactivity of Rh^I compared to Co^I is noteworthy although the variety of Rh^I species in the initial solutions does not allow a clear comparison with the Co^I complex to be made. The nature of the alkyne is also clearly of great importance in determining reactivity with these types of M^I complexes. Activation of the terminal CH carbon by the electron-withdrawing groups phenyl or CF_3 facilitates reaction whereas neither acetylene nor the straight chain alkyne hex-1-yne react with either Rh^I or Co^I complexes. The influence of electron-withdrawing groups in promoting oxidative-addition reactions of alk-1-ynes has been noted in reactions involving Ir^I π-acid derivatives [13].

Alk-1-ynes and Co^{III} compounds

McKenzie et al. [4] isolated several α-alkynyl derivatives of Co(Salen) and

Co(Sal-1,2-pn) by reacting the alkynes with the products of aerial oxidation of the Co^{II} complexes in methanol solution. This oxidation process has been claimed to yield $Co(Salen)OH \cdot H_2O$ [14] or the methoxide derivative but McKenzie [15] showed that the solid product from such a reaction is heterogeneous and contained some paramagnetic material. We have re-examined the reaction of Co^{II}(Salen) with oxygen in methanol and find that after a sufficiently long passage of oxygen no further ESR spectrum is shown by the resulting olive-brown solution, while the product obtained from solution by gentle evaporation is diamagnetic, both observations indicating conversion to Co^{III} species. However, refluxing the 'ESR' silent solution with a stream of nitrogen passing through it results in a gradual change back to the red-orange colour of the initial Co(Salen) solution and observation of the appropriate ESR signal for the complex [16].

Such solutions could be "re-oxygenated" and "deoxygenated" many times. The Co(Salen) samples prepared for use in this work [17] were not greatly soluble in methanol, but on passage of oxygen excess solid could dissolve as oxidation proceeded. "De-oxygenation" as described above caused reprecipitation of crystalline Co(Salen) from such concentrated solutions.

This behaviour is that associated with the well known reversible oxygen-carrying capacity of many Co^{II} complexes [18] and points to the formation of superoxo $\{BCo(Salen)O_2\}$ and peroxo $\{[BCo(Salen)]_2O_2\}$ compounds in this system. The major product would appear to be the diamagnetic peroxo complex when a sufficient time for reaction is allowed. The need for an appropriate Lewis base to promote reaction with oxygen is well established [18] and either water or methanol must function in that way in the present system. Pyridine promotes the formation of peroxo Co^{III}(Salen) species [18–20] and accordingly synthetic experiments were carried out in which pyridine-methanol solutions of Co^{II}(Salen) were treated with a stream of oxygen for some hours then excess of an alk-1-yne added and the reaction allowed to proceed at room temperature. Three alkynes were examined which showed a considerable difference in proton acidities decreasing in the order $CF_3C_2H > C_6H_5C_2H \gg CH_3(CH_2)_3C_2H$ [21] in order to test the scope of the reaction.

An immediate change in colour of the solution to orange occurred when 3,3,3-trifluoromethylprop-1-yne was added followed by precipitation of the sparingly soluble alkynyl $CF_3C{\equiv}CCo(Salen)py$ in high yield (90%). Phenylethyne, however, reacted slowly over several days to yield the corresponding derivative $C_6H_5C{\equiv}CCo(Salen)py$ in notably lower yield (ca. 45%). McKenzie et al. [4] did not quote yields for their preparations and in our hands the method, without the addition of pyridine, showed a slow reaction with a low final yield of unsolvated complex $C_6H_5C{\equiv}CCo(Salen)$ (ca. 20%).

Hex-1-yne showed no sign of reaction with the Co^{III} system with or without pyridine being present even after 4–5 days' reaction time.

The isolated alkynyl derivatives each displayed a sharp infra-red spectral band in the region expected for a $C{\equiv}C$ stretching frequency viz. 2160 cm^{-1} ($CF_3C{\equiv}CCo(Salen)py$), 2120 cm^{-1} ($C_6H_5C{\equiv}CCo(Salen)py$). Their ^1H NMR spectra showed only those peaks associated with the protons of Salen and the aromatic protons of the C_6H_5 group of the phenylethynyl derivative. No evidence for vinylidene protons was found.

Reactions involving phenylethyne and hex-1-yne were also carried out under more vigorous conditions. Co^{II}(Salen) was first reacted with oxygen in a mixture of pyridine and dimethylsulfoxide, the latter base being also known to promote formation of $[BCo(Salen)]_2O_2$ [20]. The appropriate alkyne was then added and the mixture heated in a sealed tube at 120°C for 1 h.

Under these conditions phenylethyne gave a high yield of the alkynyl $C_6H_5C{\equiv}CCo(Salen)py$ but hex-1-yne still failed to show evidence for reaction.

The presence of a peroxy Co^{III} complex is not essential for reaction to occur since virtually quantitative formation of $C_6H_5C{\equiv}CCo(Salen)py$ was accomplished by reacting the acetylacetonato complex, $Co^{III}(Salen)(acac)$ [22] with $C_6H_5C_2H$ in pyridine 1 DMSO at 120°C for 1 h. Acetylacetone was detected as the second product.

Some evidence was obtained also for the reaction of hex-1-yne using Co(Salen)(acac) since a very small yield of sparingly soluble product was isolated from a reaction involving that alkyne, which showed an infra-red band at 2121 cm^{-1} together with the normal features of the Co(Salen) structure. There was insufficient available for analysis.

It may thus be concluded that the synthesis of $CoC{\equiv}CR$ alkynyl derivatives by the "McKenzie" route or its modification with the use of other Co^{III} derivatives and reaction conditions is limited to alkynes of comparable or greater proton acidity than phenylethyne. The mechanism of the reaction remains unclear although the overall process may be represented as an acid displacement reaction with the

$$Co(Chel)X + HC{\equiv}CR \rightarrow Co(Chel)C{\equiv}CR + HX$$

unsaturated $C{\equiv}C$ system acting to stabilize the Co–C bond.

Experimental

Tetrahydrofuran for electrochemical measurements was purified by treatment with sodium and finally distilled in the presence of benzophenone ketyl under purified nitrogen.

Electrochemical measurements were carried out as previously described [10,23] using a PAR174A polarographic analyser for the polarographic measurements, and constant potential reductions with a working electrode of 3 × 3 cm Pt mesh and a counter electrode of Pt foil. Additional coulometric determinations were made with a BAS100. Cyclic voltammetry was performed with a PAR175 Universal Programmer in conjunction with the PAR174A unit, and a slowly growing mercury drop as the electrode because of the surface tension problems met with in THF when attempting to use a stationary hanging mercury drop [9]. Infrared spectra were measured using a Jasco IRA-1 spectrophotometer. ^1H NMR spectra were recorded on a Bruker WH-90 Spectrospin. ESR measurements were made using a Varian E12 spectrometer.

Bispyridine-N,N'-ethylenebis(salicylaldiminato)rhodium hexafluorophosphate, $[Rh(Salen)py_2]PF_6$

The preparation involved reaction of Zn(Salen) with *trans*-$Rhpy_4Cl_3$ in the presence of a small amount of zinc powder modifying the previously reported preparation of such complexes which used the free ligand and a larger amount of metallic zinc [8].

Zn(Salen) (0.42 g, 1.3 mmol) and *trans*-$[Rhpy_4Cl_2]Cl \cdot 5H_2O$ (0.61 g, 1 mmol) were dissolved in pyridine (70 ml) with heating and stirring. Close to the boiling point zinc powder (A.R. grade) (8 mg) was added to the reaction mixture. The initial yellow solution rapidly turned red on addition of zinc and darkened further on refluxing for 75 min. The mixture was cooled, filtered and concentrated under vacuum to a small volume. Excess pyridine was removed by evaporation to dryness and resolution of the residue in methanol several times. The final residue was dissolved in water and refluxed for 60 min, to decompose any $[ZnCl_3]^-$ anions present. On continued boiling a white film or precipitate of $Zn(OH)_2$ was usually observed. The resulting orange solution was filtered hot and, after cooling, was added to a column of Sephadex C25 cation exchanger, a broad orange band being formed at the head of the column. Aqueous, 0.025 *M* NaCl was then passed down the column resulting in two yellow bands being eluted, leaving the major yield of material adsorbed at the head of the column. The section of Sephadex containing this band was removed and extracted with acetone. An aqueous solution of KPF_6 was added to precipitate the product as the hydrate $[Rh(Salen)py_2]PF_6 \cdot H_2O$ yield 50%. Water of crystallization could be removed by heating at 100°C under vacuum (10^{-3} mmHg).

Found: C, 46.7; H, 3.51; N, 8.16. $C_{26}H_{24}F_6N_4O_2PRh$ calcd.: C, 46.4; H, 3.57; N, 8.33%. ^{1}H NMR ($(CD_3)SO$), 8.69 (d, 2H (HC=N)), 8.45 (q, 4H (α-H of py)), 7.99 (m, 2H (γ-H of py)) 7.56–7.00 (m, 10H (6 aromatic protons and 2, β-H of py)), 6.58, (m, 2H (2 aromatics)), 4.41 (s, 4H, (CH_2CH_2)).

Preparation of $[Rh^{I}(Salen)]$

The complex $[Rh(Salen)py_2]PF_6$ (40 mg) was suspended in dry degassed tetrahydrofuran (30 ml) under nitrogen and stirred together with 0.4% sodium amalgam (1 g) for 1 h to give a red-brown solution of the complex. The solution was filtered carefully to remove traces of amalgam and was ready for reaction.

$C_6H_5C{\equiv}CRh(Salen)py \cdot H_2O$

Phenylethyne (2 ml) was added to the solution of $[Rh^{I}(Salen)]^-$ and the mixture stirred for 5 h under nitrogen. During this time the colour of the solution slowly changed to orange. The solution was evaporated under reduced pressure and the residue dissolved in dry pyridine and stirred for a further 15 min. Addition of water (3 ml) yielded a small amount of yellow solid and an orange oil. Addition of methanol to the oil caused the precipitation of an orange solid which was filtered and washed with methanol before drying under vacuum. Yield 60%.

Found: C, 61.5; H, 4.50; N, 7.31. $C_{29}H_{26}N_3O_3Rh$ calcd.: C, 61.4; H, 4.61; N, 7.40%. ^{1}H NMR ($(CD_3)_2SO$) 8.42 (d, 2H, (HC = N)), 8.22 (d, 2H, (HC=N)), (d, 2H, (α-H of py)) 7.85 (m, 1H, (γ-H of py)) 7.5–6.40 (m, 15H, (βH of py, aromatics including Ph-C_2).

Reactions of $[Co^{I}(Salen)]^-$ with alk-1-ynes

Co^{II}(Salen) [17] (1 g) was added to dry, deoxygenated tetrahydrofuran (100 ml) under a nitrogen atmosphere and 1% sodium amalgam (7 ml) added. The mixture was stirred and reduction was complete in ca. 1 h, the solution obtained being a deep green colour. The amalgam was removed and excess (1–2 ml) of a liquid ethyne added (phenylethyne, hex-1-yne). In the case of 3,3,3-trifluoroprop-1-yne, the gas was bubbled through the Co^{I} solution until no further colour change to red-brown could be observed (1–2 min). Phenylethyne underwent slow reaction over 18–24 h, again the solution colour changing from green to red-brown.

Filtration of the solutions yielded the sparingly soluble red-orange alkynyl derivatives only in the phenyl and trifluoropropyne reactions. The phenyl complex was recovered in low yield (2–5%) and the trifluoromethyl derivative in high yield (80%) based on the initial Co complex. Addition of small amounts of water to the filtrates yielded only further small crops of the complexes. Evaporation of the filtrate from the phenylethyne reaction yielded a considerable quantity of a brown solid but infrared spectral examination failed to reveal any absorption appropriate to a C≡C linkage. Thin layer chromatographic examination of the filtrate indicated the presence of some Co^{II}(Salen) and at least a further five Co-containing species. No attempt was made to isolate individual compounds from the mixture.

The derivatives were recrystallized from ethanol as unsolvated complexes. In the presence of added pyridine to promote solubility, the mono pyridinates were obtained, the CF_3C_2 complex having a further molecule of water of crystallization.

No evidence of reaction was obtained between $[Co^I(Salen)]^-$ and hex-1-yne after reaction times of several days.

$C_6H_5C{\equiv}CCo$(Salen). Found: C, 67.5; H, 5.28; N, 6.59. $C_{24}H_{19}N_2O_2Co$ calcd.: C, 67.3; H, 5.94; N, 6.54%. ν(C≡C) (Nujol) 2120 cm^{-1}.

$C_6H_5C{\equiv}CCo$(Salen)py. Found: C, 68.7; H, 4.96; N, 8.33. $C_{29}H_{24}N_3O_2Co$ calcd.: C, 68.9; H, 4.79; N, 8.32%.

$CF_3C{\equiv}CCo$(Salen)py · H_2O. Found: C, 55.9; H, 3.91; N, 7.82; F, 10.9. $C_{24}H_{21}F_3N_3O_3Co$ calcd.: C, 55.7; H, 4.09; N, 8.12; F, 11.0%. ν(C≡C) (Nujol) 2160 cm^{-1}.

Reactions of $[py(Co^{III}(Salen)]_2O_2$ with alk-1-ynes

(a) At room temperature. Co^{II}(Salen) (1 g) was supended in methanol (100 ml) and pyridine (5 ml) added causing most of the complex to dissolve. Air was bubbled through the mixture for 24 h resulting in a dark, olive-brown solution being formed. Excess (3–4 ml) of a liquid alkyne (phenylethyne, hex-1-yne) was added to the solution and the mixture stirred at room temperature. The phenylethynyl derivative precipitated slowly over several days (max. yield 45%) whereas no reaction products could be observed with hex-1-yne after 4–5 days. Gaseous CF_3C_2H was bubbled through a similar "oxygenated" solution of Co^{II}(Salen) to produce a concentrated solution of the ethyne. A copious precipitate of the trifluoropropynyl complex was formed within several hours reaction time (max. yield 90%). The complexes were filtered off and recrystallized from ethanol/pyridine mixtures as the monopyridinates.

(b) Reactions at 120°C. Co^{II}(Salen) (0.5 g) was placed in a 50 ml Carius tube fitted with a Young tap. Dry dimethylsulfoxide (2 ml) and pyridine (2 ml) were then added together with a small magnetic stirrer bar. Air was bubbled through the brown-orange suspension for 15 min then a sample of a liquid alkyne added (0.5 ml–excess in each instance) or CF_3C_2H bubbled through the solution for several minutes to produce a concentrated solution. The tap was then closed and the tube heated at 120°C with constant stirring of the contents for 1 h. The reaction mixture, after cooling, was poured into water (50 ml) with vigorous stirring.

Virtually quantitative yields of $C_6H_5C{\equiv}CCo$(Salen)py and $CF_3C{\equiv}CCo$(Salen)py were obtained but there was no evidence for the formation of hex-1-ynyl-Co products.

Similar reactions were carried out using Co^{III}(Salen)(Acac) [22] (0.5 g) instead of Co(Salen). The complex dissolved completely in the solvent mixture. Oxygen was not bubbled through the solution but the Carius tube was not flushed with nitrogen before sealing.

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