

NOTE

Synthesis, Reactions and Catalytic Activities of a Cationic Acrylonitrile-Rhodium(I) Complex

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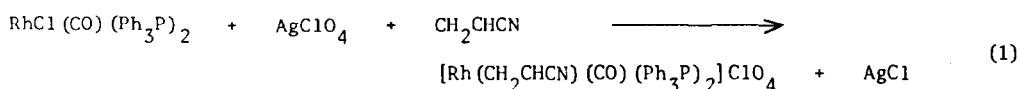
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Abstract: Reaction of $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (Ph_3P = triphenylphosphine) with AgClO_4 in acrylonitrile at 30°C produces a new cationic rhodium(I) complex, $[\text{Rh}(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ (**1**) and AgCl . The $^1\text{H-NMR}$ and IR spectra of **1** suggest that acrylonitrile is coordinated to rhodium through the π -system of the vinyl group. The complex **1** reacts with molecular hydrogen to give a propionitrile-rhodium(I) complex, $[\text{Rh}(\text{CH}_3\text{CH}_2\text{CN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ (**2**) where the coordination of propionitrile through nitrogen is suggested by the $^1\text{H-NMR}$ and IR spectral data. The coordinated acrylonitrile in **1** is readily replaced with triphenylphosphine and propionitrile to give $[\text{Rh}(\text{CO})(\text{Ph}_3\text{P})_3]\text{ClO}_4$ and **2**, respectively. The complex **1** is catalytically active for the hydrogenation and polymerization of acrylonitrile at 25°C under the atmospheric pressure of hydrogen.

The reaction of $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ with AgClO_4 in acrylonitrile produces AgCl precipitate and the clear yellow solution which is catalytically active for the polymerization of acrylonitrile under nitrogen at room temperature.¹ Subsequently, we have become interested in the reaction of the rhodium analog, $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ with AgClO_4 in acrylonitrile.

We wish to report the synthesis, reactions and catalytic activities of a new cationic rhodium(I) complex, $[\text{Rh}(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ (**1**) which has been identified by elemental analyses, conductivity measurements, $^1\text{H-NMR}$ and IR spectral data. There have been a few other cationic acrylonitrile-rhodium(I) complexes reported (e.g., $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{CH}_2\text{CHCN})]\text{ClO}_4$, $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{CH}_2\text{CHCN})(\text{Ph}_3\text{P})]\text{ClO}_4$) with their catalytic activities for the hydrogenation of olefins.²

The addition of AgClO_4 into the yellow solution of $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ in acrylonitrile under nitrogen immediately produced AgCl precipitate.³ The yellow solution obtained by the removal of AgCl turned orange within one hour and eventually dark brown within three hours at 30°C under nitrogen. The addition of hexane to this dark brown solution resulted in brown solid of $[\text{Rh}(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ (**1**) (eq. 1).⁴ The complex **1** is stable in the solid state in air and in solution under nitrogen, and soluble in polar organic solvents (acrylonitrile, chloroform, dichloromethane) but insoluble in non polar solvents (benzene, hexane).

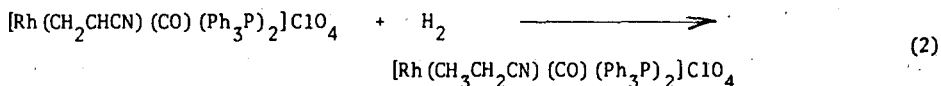


The molar conductance ($120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of 1 ($4.0 \times 10^{-5} \text{ M}$ in acrylonitrile) shows that the complex 1 is a 1:1 electrolyte.⁵

The formation of a π -bonding between acrylonitrile and rhodium is suggested by the IR spectrum of 1. The nitrile stretching frequency, ν_{CN} of acrylonitrile in 1 (2220 cm^{-1} , Nujol) is lower than that of free acrylonitrile (2230 cm^{-1}). The decrease in ν_{CN} indicates that the acrylonitrile in 1 is coordinated to rhodium through the π -system of the vinyl group since it is well known that ν_{CN} of acrylonitrile increases upon coordination to a metal through nitrogen.⁶ A very strong and broad absorption band at ca. 1100 cm^{-1} (Nujol) attributable to the anionic tetrahedral ClO_4 group⁷ supports that 1 is an ionic compound as confirmed by the conductivity data (see above). The ν_{CO} and ρ_{CH_2} (CH_2CHCN) in 1 appear at 1995 (very strong) and 950 (medium) cm^{-1} (Nujol), respectively.

The acrylonitrile hydrogens of 1 give rise to a multiplet at ca. $\delta = 5.75$ ppm (vs. TMS, in CDCl_3) shifted upfield ca. 0.25 ppm from those (at ca. $\delta = 6.0$ ppm) of free acrylonitrile. The multiplet due to the phenyl hydrogens of triphenylphosphine is seen at ca. $\delta = 7.5$ ppm. The chemical shift of acrylonitrile in 1 and the ratio (10:1) of phenyl hydrogens to acrylonitrile hydrogens clearly suggest $\text{Rh}(\text{CH}_2\text{CHCN})(\text{Ph}_3\text{P})_2$ moiety in 1. The upfield shifts (0.25 ppm) observed for the acrylonitrile hydrogens in 1 are understood in terms of the increase in electron density at acrylonitrile due to its π -acceptor character through the π -system of the vinyl group as suggested by the IR data. The low oxidation state of rhodium in 1 probably facilitates the electron flow from the metal to the π -system of the vinyl group in the coordinated acrylonitrile. The hydrogens of acrylonitrile coordinated through nitrogen show downfield shifts relative to those of free acrylonitrile.^{6,8} No complexes of coordinated acrylonitrile through the π -system of the nitrile group have been reported thus far.⁶

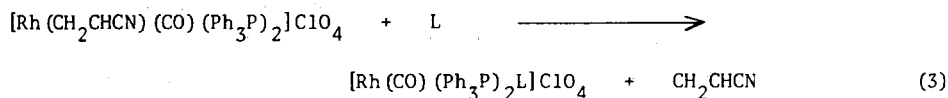
The complex 1 reacts with molecular hydrogen in chloroform at 25°C to give the propionitrile-rhodium(I) complex, $[\text{Rh}(\text{CH}_3\text{CH}_2\text{CN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ (2) (eq. 2).⁹



The IR spectral data provide the information on the nature of the bonding between metal and nitrile. It is well established that the bonding of a nitrile to a transition metal through nitrogen increases ν_{CN} relative to ν_{CN} of the nitrile uncoordinated, whereas the bonding through the π -system of the $\text{C}\equiv\text{N}$ group is characterized by a decrease in ν_{CN} .⁶ The ν_{CN} of propionitrile in 2 is seen at 2260 cm^{-1} (Nujol) while that of free propionitrile is seen at 2248 cm^{-1} ,¹⁰ which suggests that the propionitrile in 2 is coordinated through nitrogen. The ν_{CO} (1970 cm^{-1} , Nujol) observed for 2 is significantly lower than that (1995 cm^{-1}) for 1. This may be the reflection of stronger Rh-CO bond in 2 than in 1. The IR spectrum of 2 also shows a strong and broad band at 1100 cm^{-1} (Nujol) suggesting the anionic tetrahedral ClO_4 group in 2 as seen for 1.⁷

The ^1H -NMR spectrum of 2 shows the methyl hydrogens of the coordinated propionitrile at $\delta = 0.53$ ppm (triplet, vs. TMS, CDCl_3) and the methylene hydrogens at $\delta = 1.97$ ppm (quartet), while free propionitrile shows those at $\delta = 1.22$ and $\delta = 2.38$ ppm, respectively. The moiety of $\text{Rh}(\text{CH}_3\text{CH}_2\text{CN})(\text{Ph}_3\text{P})_2$ is evident in 2 from the chemical shifts of the hydrogens of propionitrile and the ratio of the phenyl hydrogens at ca. $\delta = 7.5$ ppm to the hydrogens of propionitrile. The methyl hydrogens of propionitrile in 2 are shielded more upon coordination to rhodium(I) than the methylene hydrogens ($1.22 - 0.53 = 0.69$ ppm and $2.38 - 1.97 = 0.41$ ppm, respectively). The hydrogens of saturated nitriles coordinated to d^6 transition metals (Ru(II) , Rh(III)) showed downfield shifts relative to those of the free nitriles,⁸ while those coordinated to d^8 transition metal (Ir(I)) showed upfield shifts.^{11,12} The upfield shifts observed for 2 may be due to the facile electron flow from the electron rich rhodium(I) to propionitrile. The spin coupling between ^{103}Rh and the hydrogens of coordinated propionitrile has not been observed.

Acrylonitrile in 1 is readily replaced by propionitrile or triphenylphosphine to give 2 or $[\text{Rh}(\text{CO})(\text{Ph}_3\text{P})_3]\text{ClO}_4$ ¹³ in chloroform under nitrogen at 25°C (eq. 3).



$\text{L} = \text{CH}_3\text{CH}_2\text{CN}, \text{Ph}_3\text{P}$

The reaction of 1 with molecular hydrogen to produce 2 (eq. 2) has prompted us to investigate the catalytic activity of 1 for the hydrogenation of acrylonitrile. It has been found that the acrylonitrile solution of 1 under hydrogen ($\text{P}_{\text{H}_2} = 700$ mmHg) at 25°C catalytically produces propionitrile and polyacrylonitrile. For example, a 10 ml of acrylonitrile solution of 1 (0.12 g, 0.15 mmole) under hydrogen ($\text{P}_{\text{H}_2} = 700$ mmHg) produces 7.5 mmoles of propionitrile and 0.12 g (ca. 2.3 mmoles of acrylonitrile monomer) of insoluble beige polyacrylonitrile¹⁴ for 100 hours at 25°C .

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References

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- (2) R. Uson, L. A. Oro, J. Jartigas and R. Sariego, *J. Organomet. Chem.*, **179**, 65-72 (1979).
- (3) 0.203 g of AgClO_4 (0.98 mmol), 0.675 g of $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ (0.98 mmol) and 15 ml of CH_2CHCN were used.
- (4) The brown solid was thoroughly washed with benzene. The yield was 0.687 g or 81% based on $[\text{Rh}(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$. Anal. Calcd for $\text{RhC}_{40}\text{H}_{33}\text{NC}_{10}\text{O}_5$

- P_2 : C, 59.46; H, 4.12; N, 1.73; Cl, 4.39; P, 7.67.
 Found: C, 59.21; H, 4.20; N, 1.81; Cl, 4.31; P, 7.71. The complex 1 can also be prepared by the reaction of $Rh(ClO_4)(CO)(Ph_3P)_2$ with acrylonitrile.
- (5) Molar conductance of a standard 1:1 electrolyte $[(C_3H_7)_4N]PF_6$ in acrylonitrile at 25° is $130\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$.
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- (9) 0.16 g (0.2 mmol) of 1 dissolved in 10 ml of chloroform was stirred under hydrogen ($P_{H_2} = 700\text{ mmHg}$) at 25°C for 24 hours during which time no visual change was observed. Addition of hexane (ca. 25 ml) to the solution resulted in brown solid (2) which was collected by filtration and washed thoroughly with benzene. The yield was 0.12 g or 74% based on $[Rh(CH_3CH_2CN)(CO)(Ph_3P)_2]ClO_4$.
 Anal. Calcd for $RhC_{40}H_{35}NC_{10}P_2$: C, 59.31; H, 4.35; N, 1.73; Cl, 4.38; P, 7.65.
 Found: C, 59.09; H, 4.21; N, 1.86; Cl, 4.40; P, 7.77. The molar conductance of 2 is $120\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in acrylonitrile at 25°C when $[2] = 4.0 \times 10^{-5}\text{ M}$.
 The complex 2 can also be prepared by the reaction of $RhCl(CO)(Ph_3P)_2$ with $AgClO_4$ in propionitrile under nitrogen at 30°C (refer the experimental details for the preparation of 1 in text and ref. 4).
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- (14) Polyacrylonitrile was separated by filtration and identified by the infrared spectrum. In the absence of 1, polyacrylonitrile was not obtained under the same experimental conditions (25°C , $P_{H_2} = 700\text{ mmHg}$).