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PREPARATION AND REACTIONS OF SOME METHYL ISOCYANIDE COMPLEXES OF RHODIUM

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SUMMARY

The preparation of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ and $[(CH_3NC)_4Rh][B(C_6H_5)_4]$ are reported. Oxidative addition of oxygen, tetracyanoethylene, mercuric chloride, and iodine to $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ and of methyl iodide and iodine to $[(CH_3NC)_4Rh^+]$ are described. Hydrolysis of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ yields $[(C_6H_5)_3P]_2Rh(CO)Cl$.

INTRODUCTION

Despite the current widespread interest in the reactivities of low valent d^8 transition metal complexes[1] relatively little attention has been given to the isocyanide complexes of Rh^I. The preparations of aryl isocyanide complexes of the types $(ArNC)_4Rh^+$ (ref. 2), $(ArNC)_2Rh(CO)X$[3], and $(ArNC)_2Rh(EPh_3)_2^+$ (E = P, As, Sb)[3] from $[(CO)_2RhCl]_2$ have been reported. The ability of these species to undergo oxidative addition reactions has not been explored except for a brief report that $(C_6H_5NC)_2Rh(CO)X$ does not give stable products upon oxidation with halogens[4]. Herein are reported the preparation of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ and $[(CH_3NC)_4Rh][B(C_6H_5)_4]$ and details of their behavior toward a variety of oxidizing agents.

EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR 12 spectrometer. Conductivities were measured using a Serfass conductivity bridge. Solutions of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ were prepared and handled under an atmosphere of purified nitrogen. Methyl isocyanide[5], chlorotris(triphenylphosphine)rhodium(I)[6], and chloro(1,5-cyclooctadiene)rhodium(I) dimer[7] were prepared according to existing methods.

Chloro(methyl isocyanide)bis(triphenylphosphine)rhodium(I), $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$

Under an atmosphere of purified nitrogen a solution of 0.065 g (1.6 mmole) of methyl isocyanide in 1 ml of dichloromethane was added to a solution of 1.50 g (1.63 mmole) of chlorotris(triphenylphosphine)rhodium(I) in 30 ml of dichloromethane. Oxygen-free hexane was slowly added to the solution to precipitate the complex as yellow crystals. The complex (0.76 g, 67 %) was collected by filtration. Purification was effected by recrystallization from dichloromethane/hexane; the complex decomposes upon heating above 160°. (Found: C, 65.16; H, 4.46. $C_{40}H_{36}ClN_2PRh$ calcd.: C, 64.83 H, 4.72%.)

Chlorodiiodo(methyl isocyanide)bis(triphenylphosphine)rhodium(III), $[(C_6H_5)_3P]_2Rh(CNCH_3)ClI_2$

A solution of 0.0685 g (0.267 mmole) of iodine in 30 ml of dichloromethane was added to a solution of 0.1911 g (0.271 mmole) of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ in 40 ml of dichloromethane. Fifteen ml of n-heptane was added to the brown solution. Dichloromethane was distilled from the solution until its volume was 20 ml. On cooling the complex crystallized as fine brown needles. The product was collected by filtration, recrystallized from dichloromethane/heptane, and vacuum dried at 80°; m.p. 240–247° dec. (Found: C, 47.28; H, 3.51; I, 26.03. $C_{38}H_{33}ClI_2NP_2Rh$ calcd.: C, 47.65; H, 3.47; I, 26.50%.)

Chloro(methyl isocyanide)(tetracyanoethylene)bis(triphenylphosphine)rhodium(III), $[(C_6H_5)_3P]_2Rh[C_2(CN)_4](CNCH_3)Cl$

A solution of 0.0376 g (0.294 mmole) of tetracyanoethylene in 10 ml of dichloromethane was added to a solution of 0.1899 g (0.270 mmole) of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ in 30 ml of dichloromethane. After reducing the volume of the solution to 5 ml with a rotary evaporator, n-heptane was slowly added to precipitate the product. Recrystallization from dichloromethane/heptane followed by vacuum drying yielded the product in 60% yield as fine yellow crystals; m.p. 215–228° dec. (Found: C, 63.20; H, 3.80; N, 8.24. $C_{44}H_{33}ClN_5P_2Rh$ calcd.: C, 63.51; H, 4.00; N, 8.42%.)

Adduct of chloro(methyl isocyanide)bis(triphenylphosphine)rhodium(I) with mercuric chloride, $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl\cdot HgCl_2$

A solution of 0.103 g (0.38 mmole) of mercuric chloride in 30 ml of ether was added to a solution of 0.275 g (0.39 mmole) of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ in 50 ml of dichloromethane. The solution was filtered and evaporated. The yellow crystalline product was purified by recrystallization from dichloromethane/ether; m.p. dec. above 190°. (Found: C, 45.71; H, 3.03; Cl, 11.07. $C_{38}H_{33}Cl_3HgNP_2Rh$ calcd.: C, 46.71; H, 3.41; Cl, 10.90%.)

Triiodotris(methyl isocyanide)rhodium(III), $(CH_3NC)_3RhI_3$

Methyl isocyanide (0.5 ml) was added to a solution of 0.5 g of $RhCl_3\cdot 3H_2O$ in 10 ml of water. To the resulting clear yellow solution was added 3 ml of a saturated aqueous solution of sodium iodide. The red-brown precipitate was collected by filtration and vaccum dried. Purification was effected by dissolving the product in hot dichloromethane, filtering, and precipitating the product (yield 0.1 g) as red-brown crystals by the addition of ether; the compound darkens on heating but does not melt below 250°. The complex is a non-electrolyte in *N,N*-dimethylformamide. (Found: C, 12.03; H, 1.50; N, 6.93. $C_6H_9I_3N_3Rh$ calcd.: C, 11.88; H, 1.49; N, 6.93%.)

Tetrakis(methyl isocyanide)rhodium(I) tetraphenylborate, $[(CH_3NC)_4Rh][B(C_6H_5)_4]$

From $RhCl_3\cdot 3H_2O$. A solution of 1.0 g of $RhCl_3\cdot 3H_2O$ in 40 ml of water was treated with 1.5 ml of methyl isocyanide. After standing for 30 min a solution of 1.2 g of sodium tetraphenylborate in 20 ml of methanol was added. The resulting precipitate was collected and vacuum dried. The product may be purified either by dissolving in warm (70°) *N*,*N*-dimethylformamide, filtering and adding methanol to precipitate the product or by recrystallization from dichloromethane/n-propanol. Fine yellow crystals (0.56 g, 23%) were obtained; m.p. 194–202° dec. (Found: C, 66.06; H, 5.67; N, 9.70. $C_{32}H_{32}BN_4Rh$ calcd.: C, 65.55; H, 5.50; N, 9.56%.)

From chloro(1,5-cyclooctadiene)rhodium(I) dimer. Methyl isocyanide (1.0 ml) was added to a slurry of 1.0 g of $[1,5\text{-}C_8H_{12}RhCl]_2$ in 30 ml of methanol. After dissolution of the starting material was complete, 1.5 g of sodium tetraphenylborate in 10 ml of methanol was added. The yellow precipitate was collected by filtration and vacuum dried. After purification as outlined above yellow crystals (1.9 g, 80%) identical in all respects to the product obtained from $RhCl_3 \cdot 3H_2O$ were isolated.

Diiodotetrakis(methyl isocyanide)rhodium(III) tetraphenylborate, $[(CH_3NC)_4RhI_2][B(C_6H_5)_4]$

A suspension of 0.2242 g of $[(CH_3NC)_4Rh][B(C_6H_5)_4]$ in 20 ml of dichloromethane was treated with a solution of 0.0986 g (0.389 mmole) of iodine in 20 ml of dichloromethane. The mixture was refluxed for 1 h and then taken to dryness on a rotary evaporator. The solid was recrystallized from acetone to yield the product in 80% yield as brick-red crystals; m.p. 192–197° dec. (Found: C, 45.40; H, 3.81; I, 29.53. $C_{32}H_{32}BI_2N_4Rh$ calcd.: C, 45.75; H, 3.84; I, 30.21%.)

Iodomethyltetrakis(methyl isocyanide)rhodium(III) tetraphenylborate, $[(CH_3NC)_4RhCH_3I][B(C_6H_5)_4] \cdot \frac{3}{4}CH_2Cl_2$

A suspension of 0.30 g of $[(CH_3NC)_4Rh][B(C_6H_5)_4]$ in 40 ml of dichloromethane and 5 ml of methyl iodide was refluxed for 6 h. The solution was concentrated to a volume of 10 ml by distilling off the solvent. After cooling at 0°, the product was collected by filtration. Purification by recrystallization from dichloromethane yielded the product (0.21 g, 57%) as white crystals; m.p. 134–138° dec. (Found: C, 51.50; H, 4.65; I, 15.96. $C_{33}H_{35}BIN_4Rh \cdot \frac{3}{4}CH_2Cl_2$ calcd.: C, 51.18; H, 4.65; I, 16.02%.)

Hydrolysis of chloro(methyl isocyanide)bis(triphenylphosphine)rhodium(I)

A 0.17 g sample of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ was dissolved in a mixture of 85 ml of tetrahydrofuran and 10 ml of water. The solution was refluxed, under nitrogen, for 12 h. The solution was then taken to dryness on a rotary evaporator. The solid was recrystallized from a dichloromethane/cyclohexane. The infrared spectrum of the yellow product indicated that it was largely $[(C_6H_5)_3P]Rh(CO)Cl$ admixed with a small amount of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$.

Conductivity measurements

In *N*,*N*-dimethylformamide the conductivities of 1.0 m*M* solutions of $[(CH_3NC)_4Rh][B(C_6H_5)_4]$ (Λ 44 $cm^2 \cdot mole^{-1} \cdot ohm^{-1}$), $[(CH_3NC)_4Rh(CH_3)I][B(C_6H_5)_4]$ (Λ 37), and $[(CH_3NC)_4RhI_2][B(C_6H_5)_4]$ (Λ 41) are reasonable for 1/1 electrolytes.

RESULTS AND DISCUSSION

One equivalent of methyl isocyanide reacts with $[(C_6H_5)_3P]_3RhCl$ to yield yellow $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ (I). The infrared spectrum consists, in addition to bands due to triphenylphosphine, of bands at 2980, 2920, 2140 [$\nu(C{\equiv}N)$], 1400 and 885 cm^{-1} (nujol mull) which are due to the methyl isocyanide moiety and a band at 286 cm^{-1} due to ν(Rh–Cl).

In its chemical behavior (I) resembles the well known $[(C_6H_5)_3P]_2Rh(CO)Cl$, although it is somewhat more reactive. Treatment of (I) with iodine produces $[(C_6H_5)_3P]_2Rh(CNCH_3)ClI_2$. Tetracyanoethylene (TCNE) reacts with (I) to yield $[(C_6H_5)_3P]_2Rh(TCNE)(CNCH_3)Cl$. Both of these reactions also occur with $[(C_6H_5)_3P]_2Rh(CO)Cl$[4,8]. However, (I) also reacts with mercuric chloride and oxygen, species which do not react with the carbonyl analog, $[(C_6H_5)_3P]_2Rh(CO)Cl$[1,9]. With mercuric chloride the adduct $[(C_6H_5)_3P]_2Rh(CNCH_3)ClHgCl_2$ has been isolated. Oxygen appears to react reversibly with (I) to yield an adduct which has been characterized spectroscopically. Bubbling oxygen through a dichloromethane solution of (I) causes the infrared absorption at 2140 cm^{-1} in the parent compound to decrease in intensity while a new band appears at 2201 cm^{-1}. This process is reversed upon heating the solution or purging with nitrogen. Evaporation of an oxygen-saturated solution of (I) under a stream of oxygen yields a solid whose infrared spectrum resembles that of (I) except that the isocyanide stretching frequency occurs at 2201 cm^{-1} and a new doublet is present at 895 and 890 cm^{-1} (nujol). We believe that these new bands are due to the isocyanide stretch and motion of the MO_2 ring respectively in the adduct $[(C_6H_5)_3P]_2Rh(CNCH_3)O_2Cl$. Methyl iodide reacts with (I), but it has not been possible to isolate a pure product from this reaction. The analogous reaction with $[(C_6H_5)_3P]_2Rh(CO)Cl$ yields an inseparable mixture of $[(C_6H_5)_3P]_2Rh(CO)CH_3ClI$ and $[(C_6H_5)_3P]_2Rh(COCH_3)ClI$[10].

The values for the isocyanide stretching frequencies of methyl isocyanide and of the new complexes are set out in Table 1. Coordination to Rh^I shifts ν(CN) in methyl isocyanide to a slightly lower value than that which is observed for the free methyl isocyanide. Similar decreases have been observed for other isocyanide com-

TABLE 1

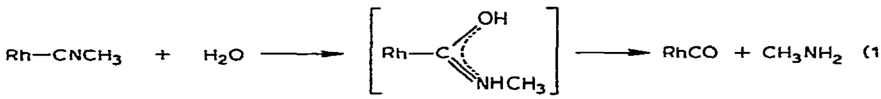
INFRARED SPECTRA

Compound	$\nu(CN)^a$ (cm^{-1})	$\nu(Rh–Cl)^b$ (cm^{-1})
$CNCH_3$	2173^c	
$[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$	2140	286
$[(C_6H_5)_3P]_2Rh(CNCH_3)O_2Cl$	2201	286
$[(C_6H_5)_3P]_2Rh(CNCH_3)ClHgCl_2$	2237	$(311, 290, 268, 230)^d$
$[(C_6H_5)_3P]_2Rh(CNCH_3)(TCNE)Cl$	2238 sh, 2231	309, 323
$[(C_6H_5)_3P]_2Rh(CNCH_3)I_2Cl$	2244	304
$[(CH_3NC)_4Rh][B(C_6H_5)_4]$	2197	
$[(CH_3NC)_4RhI_2][B(C_6H_5)_4]$	2265	
$[(CH_3NC)_4Rh(CH_3)I][B(C_6H_5)_4]$	2252	
$(CH_3NC)_3RhI_3$	2242, 2272	

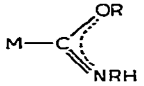
[a] Fluorocarbon mull. [b] Nujol mull. [c] Dichloromethane solution. [d] These are probably due to Hg–Cl and Rh–Cl stretching modes.

plexes of low valent metal ions. Oxidation of (I) causes an increase in ν(CN) to values which are greater than that of free methyl isocyanide. This increase in ν(CN) is caused by the decreased back-donation by the metal in the oxidized species. The carbonyl stretching frequencies in $[(C_6H_5)_3P]_2Rh(CO)Cl$ and $[(C_6H_5)_3P]Ir(CO)Cl$ are similarily increased upon oxidative addition. The increases in ν(CN) in the isocyanide complexes follow the same trend as found for the increases in ν(CO) in the carbonyl complexes. Thus in $[(C_6H_5)_3P]_2Rh(CNCH_3)ClX$ and $[(C_6H_5)_3P]Ir(CO)ClX$, both ν(CN) and ν(CO) increase as a function of X in the following way $O_2 < HgCl_2 < TCNE < I_2$.

The most unusual reaction of (I) is its hydrolysis. Refluxing a solution of (I) in 10% aqueous tetrahydrofuran results in the formation of $[(C_6H_5)_3P]_2Rh(CO)Cl$. We suspect that this transformation is initiated by nucleophilic attack by water or hydroxide on the coordinated isocyanide [eqn. (1)]. Similar attack on coordinated isonitriles by alcohols to yield stable products containing the unit (II) is well established[11]. Alcohols also react with (I) but $[(C_6H_5)_3P]_2Rh(CO)Cl$ rather than a product containing the unit (II) is obtained. The hydrolysis of (I) to yield a carbonyl complex contrasts with the other known cases of hydrolysis of metal isocyanide complexes in which a metal cyano complex and an alcohol are formed[12]. The formation of a carbonyl complex in this case is undoubtedly due in part to the well known ability of Rh^I to act as a carbonyl abstraction reagent.



(1)



(II)

Methyl isocyanide reacts with chloro(1,5-cyclooctadiene)rhodium dimer to yield the yellow cation $(CH_3NC)_4Rh^+$ which has been isolated as the tetraphenylborate salt. This complex can also be prepared from rhodium trichloride and an excess of methyl isocyanide. In this reaction, methyl isocyanide probably also serves as the reducing agent. Initially substitution products of Rh^{III} are formed as shown by the isolation of $Rh(CNCH_3)_3I_3$.

The cation $(CH_3NC)_4Rh^+$ also undergoes oxidative addition reactions. With iodine, red $(CH_3NC)_4RhI_2^+$ is formed. Methyl iodide adds to $(CH_3NC)_4Rh^+$ without methyl migration to yield $(CH_3NC)_4RhCH_3I^+$. In both cases oxidative addition results in an increase in ν(CN) in the product. The observation of only a single isocyanide stretching frequency in both of the oxidized species suggest that the planar arrangement of isocyanide ligands is maintained upon oxidation. Oxygen does not react with $(CH_3NC)_4Rh^+$.

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