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TETRAPHENYLBORATE COMPLEXES OF RHODIUM(I)

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Summary

Addition of $B(C_6H_5)_4^-$ as precipitating counteranion to cationic four-coordinate rhodium(I) complexes with nitrogen donor ligands of the type $[(NBD)RhL_2]^+$ results in a competition between coordination by the tetraphenylborate group (via π-interaction of an arene ring) and the nitrogen donor ligands. The stoichiometry of the precipitated complexes depends on the nature of these ligands.

Introduction

It is well known that reaction of the dimeric diolefin—rhodium(I) chloride complexes with uncharged monodentate or bidentate ligands in alcohols leads to the formation of cationic complexes [1—5]. These cationic complexes can be isolated by addition of a suitable anion as PF_6^-, BF_4^-, ClO_4^- or $B(C_6H_5)_4^-$. However, with the latter anion the tetraphenylborate group can be coordinated to the metal by π-interaction of an arene ring [2,6,7]. We described below the use of $B(C_6H_5)_4^-$ as precipitating counteranion for cationic rhodium(I) norbornadiene complexes containing nitrogen donor ligands.

Results and discussion

The results are summarized in Scheme 1.

The results indicate that precipitation of cationic complexes of the type I (Process A) occurs when the nitrogen donor ligands show some π-acceptor capacity, as in 1,10-phenantroline or 2,2'-bipyridine. When weak ligands with low π-acidity are used, e.g. nitriles or aniline, product II is formed (Process B).

If pyridine is used as a ligand, Process A takes place but this does not occur

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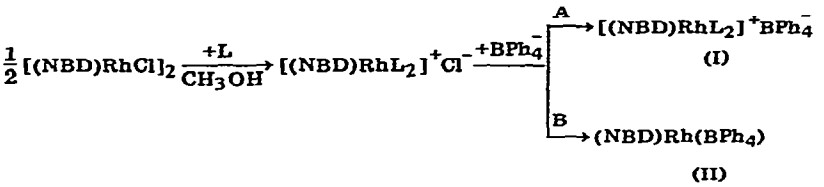
SCHEME 1



Process A: L_2 = 1,10-phenantroline, 2,2'-bipyridine; L = pyridine, 4-ethylpyridine, 3-methylpyridine, 4-methylpyridine, isoquinoline.
Process A + B: L = 2-methylpyridine, 2,4-dimethylpyridine.
Process B: L_2 = succinonitrile, malononitrile; L = acetonitrile, phenylacetonitrile, benzonitrile, aniline, 2-benzylpyridine, 2-ethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine, quinoline.

with sterically hindered ligands such as 2-benzylpyridine or 2-ethylpyridine, and the zwitterionic derivative II is precipitated. In contrast 4-ethylpyridine, which has a similar donor strength, gives the cationic complex I, probably because of the absence of steric hindrance. With less bulky substituents present as in 2-methylpyridine or 2,4-dimethylpyridine, mixtures of the two compounds, I and II, were obtained. In the case of 2,4-dimethylpyridine selective preparation of the arene complex II or the cationic complex $[(NBD)Rh(2,4\text{-}(CH_3)_2py)_2]^+BPh_4^-$ was possible by changing the reaction conditions.

Quinoline and isoquinoline show a differing behaviour. Under the same conditions the former affords the arene derivative, II, while the latter gives the cationic complex $[(NBD)Rh(iquin)_2]^+BPh_4^-$. Isoquinoline ($pK_a$ 5.42) has a greater donor strength than quinoline (pK_a 4.89), and steric hindrance in complexes of the type I should be lower for the isoquinoline ligand.

The analytical data for the cationic tetraphenylborate complexes are shown in Table 1. The products are yellow microcrystalline compounds, while the

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES $[(NBD)RhL_2]^+BPh_4^-$

L or (L—L)	Found (calcd.) (%)			Formula
	C	H	N	
Pyridine	73.62 (73.23)	6.03 (5.70)	3.97 (4.18)	$C_{41}H_{38}N_2BRh$
4-Ethylpyridine	75.87 (74.18)	6.92 (6.36)	4.24 (3.84)	$C_{45}H_{46}N_2BRh$
3-Methylpyridine	74.90 (73.72)	6.34 (6.04)	3.73 (4.00)	$C_{43}H_{42}N_2BRh$
4-Methylpyridine	74.79 (73.72)	6.24 (6.04)	3.93 (4.00)	$C_{43}H_{42}N_2BRh$
2,4-Dimethylpyridine	75.32 (74.18)	6.10 (6.36)	3.68 (3.84)	$C_{45}H_{46}N_2BRh$
Isoquinoline	76.47 (76.17)	5.53 (5.49)	3.86 (3.65)	$C_{59}H_{42}N_2BRh$
1,10-Phenantroline	74.35 (74.36)	5.35 (5.22)	3.96 (4.03)	$C_{43}H_{36}N_2BRh$
2,2'-Bipyridine	73.71 (73.45)	5.69 (5.41)	4.45 (4.18)	$C_{41}H_{36}N_2BRh$

1,10-phenantroline and the 2,2'-bipyridine complexes are orange-red. The IR spectra of the cationic complexes show two strong bands in the region 1350—1500 cm^{-1}. These result from in-plane skeletal C—C stretching modes of the phenyl ring of uncomplexed tetraphenylborate ion [6]. The bands due to coordinated NBD ligand, along with those due to the relevant N-donor, were observed in all cases.

When process B takes place, microanalysis and the IR spectrum showed the product to be the arene derivative (NBD)Rh(BPh_4), previously described by Schrock and Osborn [6]. Most of the cationic complexes having ligands which favour Process B in the presence of BPh_4^-, can be isolated as ClO_4^- or BF_4^- complexes [8—10], where no significant interaction between cation and anion has been observed. Thus addition of $NaClO_4$ to a solution of $[(NBD)RhCl]_2$ and quinoline in methanol leads to the precipitation of the complex $[(NBD)Rh(quin)_2]^+ClO_4^-$. Yield 85%. (Found: C, 54.71; H, 4.31; N, 5.37. $C_{25}H_{22}ClN_2O_4Rh$ calcd.: C, 54.32; H, 4.01; N, 5.07%).

Experimental

Starting materials

$[(NBD)RhCl]_2$ was prepared as described by Abel et al. [11] and recrystallized from dichloromethane/methanol.

The reactions were carried out in methanol at room temperature in the air.

Preparation of $[(NBD)RhL_2]^+BPh_4^-$ complexes (L_2 = 1,10-phenantroline, 2,2'-bipyridine; L = pyridine, 4-ethylpyridine, 3-methylpyridine, 4-methylpyridine and isoquinoline)

In a typical procedure 38.2 mg (0.083 mmol) of $[(NBD)RhCl]_2$ was suspended in 2 ml of methanol, and 42.8 mg (0.331 mmol) of isoquinoline was added to yield a yellow solution. This was allowed to stand for a few minutes, then $NaBPh_4$ (56.0 mg, 0.164 mmol) in 2 ml of methanol was added, and stirring was continued for 10 minutes. The suspension was filtered and the solid washed with methanol/water and diethyl ether and air dried. Yield 75%.

The other complexes were prepared similarly.

Reactions yielding the (NBD)Rh(BPh_4) complex

When the above method was used with N-donor ligands as succinonitrile, malononitrile, acetonitrile, phenylacetonitrile, benzonitrile, aniline, 2-benzylpyridine, 2-ethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine and quinoline, the same pale-yellow microcrystalline complex was obtained. Coordination of the tetraphenylborate group to the metal via a π-interaction was evident from the presence of four strong bands in the region 1350—1500 cm^{-1}, and the elemental analyses and spectral properties were consistent with formulation of all the products as (NBD)Rh(BPh_4).

In a typical reaction $[(NBD)RhCl]_2$ (35.6 mg, 0.077 mmol) was placed in 2 ml of methanol, phenylacetonitrile (36.0 mg, 0.308 mmol) was added, and the mixture was stirred vigorously to yield a yellow solution. $NaBPh_4$ (52.8 mg, 0.154 mmol) in 2 ml of methanol was added causing immediate precipitation of a pale-yellow material. The product was filtered off, washed with methanol/

water and diethyl ether, and air dried. The analysis agreed with the formulation (NBD)Rh(BPh_4). (Found: C, 73.41; H, 5.82. $C_{31}H_{28}BRh$ calcd.: C, 72.40; H, 5.49%).

Reaction of [(NBD)Rh(2,4-$(CH_3)_2$py)$_2$]$^+Cl^-$ solutions with $NaBPh_4$

(i) [(NBD)RhCl]$_2$ (30.0 mg, 0.065 mmol) and 2,4-$(CH_3)_2$py (27.8 mg, 0.259 mmol) were dissolved in 2 ml of methanol to yield a yellow solution of [(NBD)-Rh(2,4-$(CH_3)_2$py)$_2$]$^+Cl^-$. After 5 minutes $NaBPh_4$ (44.8 mg, 0.131 mmol) in 2 ml of methanol was added, and stirring was continued for 10 minutes. The suspension was filtered, and the solid was washed with methanol/water and diethyl ether and air dried. The analysis and IR spectrum showed it to be the arene derivative, II. Yield 75%.

(ii) 30.0 mg (0.065 mmol) of [(NBD)RhCl]$_2$ was suspended in 2 ml of methanol and 186.0 mg (1.736 mmol) of 2,4-$(CH_3)_2$py was added, to yield a yellow solution. This was allowed to stand for 5 minutes then $NaBPh_4$ (45.0 mg, 0.132 mmol) in 2 ml of methanol was added, and the suspension immediately filtered. The solid was washed with methanol/water and diethyl ether, air dried, and identified as the cationic complex [(NBD)Rh(2,4-$(CH_3)_2$py)$_2$]$^+$-BPh_4^- from its analysis (Table 1) and IR spectrum. Yield 72%.

(iii) When the reaction was carried out as above, with the same amounts of starting materials but with stirring continued for 10 minutes after the addition of $NaBPh_4$, the IR spectrum of the product showed the presence of both the cationic and arene complexes, I and II.

Reaction of [(NBD)Rh(2-CH_3py)$_2$]$^+Cl^-$ solutions with $NaBPh_4$

(i) 30.1 mg (0.065 mmol) of [(NBD)RhCl]$_2$ was suspended in 2 ml of methanol and 24.2 mg (0.260 mmol) of 2-CH_3py was added, to yield a yellow solution of [(NBD)Rh(2-CH_3py)$_2$]$^+Cl^-$, which was allowed to stand for 5 minutes. $NaBPh_4$ (44.9 mg, 0.131 mmol) in 2 ml of methanol was added, and stirring was continued for 10 minutes. The suspension was filtered, and the solid was washed with methanol/water and diethyl ether, and air dried. The analysis and IR spectrum showed it to be the arene derivative. Yield 78%.

(ii) The reaction was carried out as above, but using 30.0 mg (0.065 mmol) of [(NBD)RhCl]$_2$ and 188.0 mg (2.019 mmol) of 2-CH_3py. After addition of 45.0 mg (0.132 mmol) of $NaBPh_4$, the suspension formed was immediately filtered. The IR spectra of the reaction product showed the presence of both the cationic and arene complexes, I and II.

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