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PREPARATION AND CATALYTIC ACTIVITY OF CATIONIC RHODIUM TETRAFLUOROBENZOBARRELENE COMPLEXES WITH NITROGEN AND PHOSPHORUS DONOR LIGANDS

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Summary

The preparation and properties of twenty five new cationic rhodium(I) complexes with tetrafluorobenzobarrelene and mono- or bidentate nitrogen or phosphorus donor ligands are described. The complexes with tertiary phosphines show high selectivities in the hydrogenation of 1-hexyne and several diolefins towards monoolefins. The dependence of the reduction rate upon the basicity of the phosphine has been studied.

Introduction

Several types of cationic rhodium(I) diolefin complexes with nitrogen or phosphorus donor ligands have been described in recent years [1]. Some of these complexes react with molecular hydrogen in coordinating solvents to give species which are active homogeneous catalysts. In these reactions the diolefin is completely eliminated as an alkane, but the rate of the reductive elimination markedly depends on the type of the coordinated diolefin [2].

In this paper we describe a family of cationic complexes of rhodium(I) with tetrafluorobenzobarrelene(tetrafluorobenzobicyclo[2,2,2]octatriene, TFB), in order to study the influence of the rather electron-withdrawing character of the tetrafluorobenzobarrelene ligand on its coordinating ability towards the rhodium atom. The synthesis of this ligand along with some neutral rhodium(I) complexes has been reported by Massey et al. [3,4].

Results and discussion

Preparation and properties

It has been previously reported [4] that no reaction takes place when ethanol solutions of $[RhCl(TFB)]_2$ are treated with silver nitrate. Nevertheless in acetone the solvated complex $[Rh(TFB)(Me_2CO)_x]ClO_4$ can be prepared by the

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES AND YIELDS OF CATIONIC TETRAFLUOROBENZOBARRELENE COMPLEXES OF RHODIUM(I)

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
	C	H	N		
[Rh(TFB)(amquin)]ClO$_4$	44.71 (44.04)	2.79 (2.46)	4.82 (4.89)	126	46
[Rh(TFB)(tmen)]ClO$_4$	39.78 (39.69)	3.94 (4.07)	5.51 (5.14)	131	79
[Rh(TFB)(diquin)]ClO$_4$	52.86 (52.61)	2.93 (2.65)	4.16 (4.09)	127	53
[Rh(TFB)(dipy)]ClO$_4$	44.94 (45.19)	2.51 (2.41)	5.22 (4.79)	145	82
[Rh(TFB)(phen)]ClO$_4$	46.46 (47.35)	2.61 (2.32)	4.69 (4.60)	137	86
[Rh(TFB)(PhNH$_2$)$_2$]ClO$_4$	46.38 (46.89)	3.42 (3.28)	4.15 (4.55)	125	26
[Rh(TFB)(MeCN)$_2$]ClO$_4$	37.24 (37.63)	2.29 (2.37)	5.05 (5.49)	133	72
[Rh(TFB)(PhCN)$_2$]ClO$_4$	48.03 (49.19)	2.44 (2.54)	4.25 (4.41)	140	68
[Rh(TFB)(py)$_2$]ClO$_4$	45.83 (45.03)	3.11 (2.75)	4.25 (4.77)	135	69
[Rh(TFB)(2-Mepy)$_2$]ClO$_4$	46.11 (46.89)	3.33 (3.28)	4.73 (4.55)	145	65
[Rh(TFB)(2-Etpy)$_2$]ClO$_4$	47.62 (48.58)	3.81 (3.76)	4.52 (4.36)	137	40
[Rh(TFB)(2,4-Me$_2$py)$_2$]ClO$_4$	48.87 (48.58)	3.95 (3.76)	4.45 (4.36)	138	42
[Rh(TFB)(PPh$_2$Et)$_2$]ClO$_4$	55.83 (56.06)	4.30 (4.24)	—	134	81
[Rh(TFB){P(p-MeOC$_6$H$_4$)$_3$}$_2$]ClO$_4$	56.81 (57.23)	4.30 (4.27)	—	125	78
[Rh(TFB){P(p-MeC$_6$H$_4$)$_3$}$_2$]ClO$_4$	63.03 (62.53)	5.19 (4.66)	— —	120	57
[Rh(TFB){P(m-MeC$_6$H$_4$)$_3$}$_2$]ClO$_4$	63.05 (62.53)	4.99 (4.66)	— —	112	54
[Rh(TFB){P(p-FC$_6$H$_4$)$_3$}$_2$]ClO$_4$	54.58 (54.33)	2.91 (2.85)	— —	127	41
[Rh(TFB){P(p-ClC$_6$H$_4$)$_3$}$_2$]ClO$_4$	50.07 (49.71)	2.97 (2.61)	— —	122	87
[Rh(TFB)(dipy)]BPh$_4$	68.86 (68.68)	4.13 (4.26)	3.62 (3.48)	92	70
[Rh(TFB)(phen)]BPh$_4$	69.59 (69.58)	4.26 (4.13)	3.32 (3.38)	100	65
[Rh(TFB)(diphos)]BPh$_4$	69.83 (71.14)	4.84 (4.81)	— —	85	40
[Rh(TFB)(PPh$_3$)$_2$]BPh$_4$	74.06 (73.73)	4.07 (4.81)	— —	87	56
[Rh(TFB){P(p-MeOC$_6$H$_4$)$_3$}$_2$]BPh$_4$	69.03 (69.24)	4.89 (5.06)	— —	78	58
[Rh(TFB){P(p-MeC$_6$H$_4$)$_3$}$_2$]BPh$_4$	74.48 (74.53)	5.46 (5.45)	— —	81	52
[Rh(TFB){P(m-MeC$_6$H$_4$)$_3$}$_2$]BPh$_4$	74.58 (74.53)	5.49 (5.45)	— —	78	50

precipitation of the chlorine atoms of the dimer as silver chloride [5]. This intermediate reacts with a stoichiometric amount of the monodentate or bidentate ligands to give cationic complexes of the types $[Rh(TFB)L_2]ClO_4$ and $[Rh(TFB)(L—L)]ClO_4$. The ligands used were: 8-aminoquinoline (amquin) *N,N,N′,N′*-tetramethylethylenediamine (tmen), 2,2′-diquinolyl (diquin), aniline, nitriles, pyridines and several tertiary phosphines (Table 1).

An alternative route involves the addition of one mol of the bidentate ligand or two mols of the monodentate ligands to acetone solutions of $[Rh(TFB)_2]$-ClO_4 (prepared by the reaction of $[RhCl(TFB)]_2$ with $AgClO_4$ in the presence of an excess of TFB). The ligands used were: alkylpyridines, 2,2′-dipyridyl (dipy), 1,10-phenanthroline (phen) and 8-aminoquinoline (amquin).

Furthermore, new complexes of the general formulae $[Rh(TFB)L_2]BPh_4$ or $[Rh(TFB)(L—L)]BPh_4$, were prepared by the reaction indicated in eq. 1.

$$\tfrac{1}{2}[RhCl(TFB)]_2 + 2\,L(\text{or } L{-}L) + NaBPh_4 \rightarrow [Rh(TFB)\,L_2]\,BPh_4 + NaCl \qquad (1)$$

Complexes with nitrogen donor ligands are generally yellow, but the complexes of dipyridine or phenanthroline are orange-red and the complex of diquinolyl dark-red. Complexes with phosphorus donor ligands are orange or yellow-orange. Table 1 gives the analytical data and yields for the isolated complexes. All of them behave as 1 : 1 electrolytes in acetone. The perchlorate complexes give values of 110—145 $ohm^{-1}\ cm^2\ mol^{-1}$, whilst the lower values for the tetraphenylborate complexes (78—100 $ohm^{-1}\ cm^2\ mol^{-1}$) are due to the lower mobility of the bulky BPh_4^- anion [6].

The IR spectra of the complexes show absorptions characteristic of the perchlorate and tetraphenylborate anions [7,8], along with bands due to the coordinated TFB (1500s, 1300s, 1040s, 885m, 850m) and the auxiliary ligands.

Bubbling carbon monoxide at ordinary pressure through solutions of some representative cationic organocomplexes caused displacement of TFB and the formation of species of the types *cis*-$[Rh(CO)_2(N\text{-donor})_2]A$ [9—13] and $[Rh(CO)_3(P\text{-donor})_2]A$ [14,15], previously prepared by displacement of other coordinated diolefins in related cationic complexes.

In general, the chemistry and properties of cationic complexes of rhodium(I) with this particular solid diolefin are very similar to those previously observed for 1,5-cyclooctadiene or 2,5-norbornadiene ligands. Nevertheless, its strong IR absorptions allow unequivocal detection, and the known tendency towards formation of oils with these types of complexes is greatly reduced with this diolefin. All the complexes described in this paper are air-stable. Most of them decompose before melting and the decomposition temperatures are higher than those observed for analogous cyclooctadiene or norbornadiene complexes, in the cases where these are known.

Catalytic activity

Osborn et al. have studied the catalytic activity of cationic species of the type $[M(diolefin)L_2]^+$ (M = Rh and Ir; L = PR_3) in coordinating solvents, such as ethanol, acetone or tetrahydrofuran [2,16—18]. The rates of reduction reported for $[Rh(diolefin)(PPh_{3-x}Me_x)_2]^+$ complexes depend on the type of phosphine, but is difficult to elucidate the relative importance of steric and electronic factors. On the other hand, Crabtree [19] has recently shown that dichloromethane solutions of cationic diolefin iridium(I) complexes in the presence of olefin constitute hydrogenation catalysts of unprecedented activity.

Our major aim was to study the catalytic activity of $[Rh(TFB)\{P(p\text{-}RC_6H_4)_3\}_2]ClO_4$ complexes in dichloromethane. Since the substituent R (R = MeO, Me, F or Cl) in the $p\text{-}RC_6H_4$ group causes a progressive decrease in the basicity of the phosphine [20] without steric effects, it will be possible to examine the influence of this factor on the catalytic activity of these complexes. Dichloromethane solutions of these complexes react with molecular hydrogen (1 atm. 20°C), with reduction of the coordinated TFB to H_4TFB (proved by mass spectrometry). Generally, hydrogenation experiments were carried out by admission of hydrogen in the dichloromethane solution of the complex containing the appropriate substrate.

The catalytic hydrogenation of 1-heptene with these complexes shows the dependence of the reduction rate on the basicity of the phosphine. So for the less basic phosphine ($P(p\text{-}ClC_6H_4)_3$) the ITN (initial turnover number, mol H_2 (mol Rh)$^{-1}$ min^{-1}) shows a value of 5.1, whilst for the more basic triarylphosphine ($P(p\text{-}MeOC_6H_4)_3$) the ITN value is 12.8. Under the same conditions the complex with PPh_2Et ligands has a value of 14.3. The reduction rates in dichloromethane are higher than those in oxygen donor solvents. Generally, the tendency to deactivation is greater for the less basic phosphines. Along with the hydrogenation, the complexes also cause rapid isomerization of the olefins. For L = PPh_2Et the 1-hexene has completely disappeared after 5 min and analysis by GLC shows 64% hexane, 24% *trans*-2-hexene and 12% *cis*-2-hexene.

Table 2 lists the results of the catalytic hydrogenation of 1-hexyne and several diolefins, along with the maximum percentage of the corresponding monoolefin formed by hydrogenation. No clear correlation between reduction rate or selectivity and basicity of the phosphine was found in the hydrogenation of 1-hexyne. Probably the selectivity originates in the displacement of 1-hexene by 1-hexyne, and only when the 1-hexyne concentration is very low can the 1-hexene isomerize or be hydrogenated to hexane (Fig. 1). Similar behaviour has been previously observed by Schrock and Osborn in acetone or 2-methoxyethanol [17], but deactivation was frequently observed with 1-hexyne while the catalysts are more stable in the reduction of 2-hexyne. Some comparative experiments that we have performed in acetone show that

TABLE 2

THE HYDROGENATION OF 1-HEXYNE AND DIOLEFINS WITH $[Rh(TFB)L_2]ClO_4$ COMPLEXES

	Ligand (L)	Initial turnover number (ITN)(min^{-1})[a] (Maximum % monoolefins)				
		1-hexyne	isoprene	1,4-cyclohexadiene	1,3-cyclohexadiene	2,5-norbornadiene
↑ basicity	PPh_2Et	41.7 (89)	12.5 (90)	3.6 (82)	6.3 (100)	16.1 (94)
	$P(p\text{-}MeO\text{-}C_6H_4)_3$	41.7 (96)	1.4 (70)	2.9 (90)	3.5 (100)	8.3 (62)
	$P(p\text{-}Me\text{-}C_6H_4)_3$	36.4 (92)	1.3 (60)	2.8 (94)	6.3 (96)	11.5 (65)
	$P(p\text{-}F\text{-}C_6H_4)_3$	43.8 (98)	1.1 (73)	1.0 (94)	8.6 (100)	45.4 (94)
	$P(p\text{-}Cl\text{-}C_6H_4)_3$	22.2 (82)	0.9 (80)	0.6 (89)	10.5 (100)	45.5 (95)

[a] Mol H_2 (mol Rh)$^{-1}$ min^{-1}.

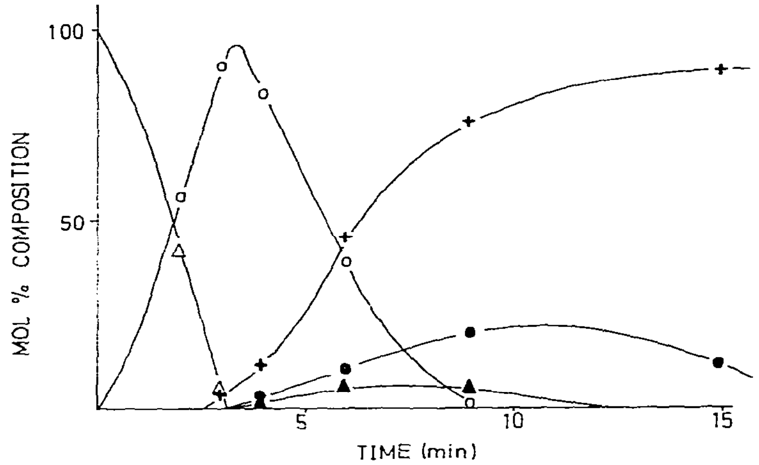

Fig. 1. The catalytic hydrogenation of 1-hexyne in dichloromethane with [Rh(TFB){P(p-MeOC$_6$H$_4$)$_3$}$_2$]ClO$_4$. 1-hexyne (△), 1-hexene (○), *trans*-2-hexene (●), *cis*-2-hexene (▲), hexane (+).

the selectivity is very similar to that observed in dichloromethane, but the reduction rate is lower.

Table 1 lists the results of the catalytic hydrogenation of isoprene. It can be observed that the rate of reduction of the diolefin increases with the basicity of the relevant triarylphosphine. Some tendency to deactivation was generally observed. The complexes with less-basic phosphines initially favour 1,4 addition of hydrogen, whilst with more basic phosphines 1,2 addition is favoured and terminal monoolefins are formed. When the concentration of isoprene is very low the terminal monoolefins isomerize to the internal olefins.

For the hydrogenation of 1,4-cyclohexadiene a direct relationship between reduction rate and basicity of the phosphine can again be observed. Cyclohexene is formed with a selectivity of 82—94%. A similar selectivity has been previously found for $[\mathrm{Ir(COD)}\{\mathrm{P}(p\text{-RC}_6\mathrm{H}_4)_3\}_2]\mathrm{ClO}_4$, but the rate is considerably higher for the iridium catalysts [21].

It is noteworthy, that when 1,3-cyclohexadiene is hydrogenated a reverse relation between reduction rate and basicity is observed, along with a high selectivity. Thus, the less basic triarylphosphine gives the higher ITN (Table 2). The same relation can be observed for the reduction of 2,5-norbornadiene to norbornene. This result is analogous to that found, by Schrock and Osborn [18], for the reduction of 2,5-norbornadiene in acetone by $[\mathrm{Rh(NBD)L_2}]^+$ species. These authors consider that the rate determining step of catalytic NBD hydrogenation is the reaction of the H_2 with the $[\mathrm{Rh(NBD)L_2}]^+$ species. We have checked that TFB is, in fact, displaced by excess of NBD, according to eq. 2.

$$[\mathrm{Rh(TFB)}\{\mathrm{P}(p\text{-RC}_6\mathrm{H}_4)_3\}_2]\,\mathrm{ClO}_4 + \mathrm{NBD} \rightarrow [\mathrm{Rh(NBD)}\{\mathrm{P}(p\text{-RC}_6\mathrm{H}_4)_3\}_2]\,\mathrm{ClO}_4 + \mathrm{TFB} \qquad (2)$$

According to previous proposals, our observations suggest that, depending on the substrate, the so-called unsaturated and hydride routes [18] must be present in varying degrees. In fact, when a direct relation between reduction rate and basicity of the phosphine is observed (1-hexene, isoprene, 1,4-cyclohexadiene) the catalytic solutions are pale-yellow, while when a reverse relation is found (1,3-cyclohexadiene, 2,5-norbornadiene) they are orange, the typical colour for $[Rh(diolefin)L_2]^+$ species when $L = PR_3$ [18].

As expected, $[Rh(TFB)(PPh_2Et)_2]ClO_4$ catalyses the reduction of 1% aqueous acetone, but no activity was observed for the homologous $[Rh(TFB)\{P(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$ complex, probably due to the lower basicity of the triarylphosphine [22].

Some $[Rh(diolefin)(N\text{-}donor)_2]ClO_4$ complexes have been reported to show catalytic activity [1,13]. We have studied some hydrogenations using $[Rh(TFB)(N\text{-}donor)_2]ClO_4$ complexes as catalysts under the conditions used for $[Rh(TFB)(PR_3)_2]ClO_4$ complexes (the olefin was added before hydrogen was admitted). In these conditions, no hydrogenation was observed, or the rate of hydrogenation was very slow, until some rhodium metal was formed by decomposition of the complex.

The $[Rh(diolefin)(PR_3)_2]ClO_4$ complexes generally show a higher catalytic activity in dichloromethane than in oxygen-donor solvents. Some of them have a tendency to become deactivated, the complex with $P(p\text{-}MeOC_6H_4)$ being the most stable.

Experimental

The C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer; the IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets; conductivities were measured in approx. 5×10^{-4} *M* acetone solutions with a Philips 9501/01 conductimeter.

Table 1 lists the analytical results, conductivities and yields for the novel complexes.

The catalytic behaviour was examined in a conventional hydrogenation apparatus provided with a septum. The reactants were introduced into the reaction flask in the following order: solution of the catalyst, substratum (3 mmol), hydrogen (initial pressure: 1 atm). A 100 : 1 ratio of substrate to catalyst and 15 ml dichloromethane as solvent were used. The rates were determined by analyzing the products in a Perkin-Elmer 3920B chromatograph. The peak areas were measured with a Minigrator Computing Integrator.

Preparation of complexes of the type $[Rh(TFB)(N\text{-}donor)_2]ClO_4$

i) A mixture of $[RhCl(TFB)]_2$ [4] and $AgClO_4$ (stoichiometric amounts) was stirred in acetone for 30 min at room temperature and then filtered through kieselguhr. The filtrate was added to an acetone solution of the appropriate mono- or bidentate nitrogen donor ligand, and the resulting solution was evaporated to 3—4 ml and crystallization was induced by the addition of ether. The precipitated solid was recrystallized from dichloromethane-ether.

ii) An alternative route was the addition of the ligand to an acetone solution of $[Rh(TFB)_2]ClO_4$ [5]. The resulting complexes were precipitated by addition of ether.

Preparation of complexes of the type $[Rh(TFB)(P\text{-}donor)_2]ClO_4$

$[RhCl(TFB)_2]$ [4] was treated with $AgClO_4$ in acetone for 15 min at room temperature and the appropriate phosphorus donor ligand was then added. Stirring was continued for another 15 min then the precipitated silver chloride was filtered off through kieselguhr and the orange coloured filtrate was evaporated to 2—3 ml. The complexes were precipitated by addition of ether and recrystallized from dichloromethane-ether.

Preparation of complexes of the type $[Rh(TFB)L_2]BPh_4$

A methanol suspension of the dimeric complex $[RhCl(TFB)]_2$ [4] and the stoichiometric amount of the relevant ligand was stirred for 1 hour whereupon the calculated amount of $NaBPh_4$ was added. The suspension was filtered and the solid washed with methanol-water (1 : 1) and diethyl ether and air dried.

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