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Dinuclear Rhodium(I) Compounds Containing Diolefins and the 1,6-Bis(2′-benzimidazolyl)-2,5-dithiahexane Ligand

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The reactions of 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane (LH_2) *with* $[RhCl(diolefin)]_2$ *and with* $[Rh(diolefin)_2]^+$ *yield dinuclear compounds of formula* $[Rh_2Cl_2(diolefin)_2(LH_2)]$ *and* $[Rh_2(diolefin)_2(LH_2)_2]^{2+}$ *respectively. Used diolefins are tetrafluorobenzobarrelene (TFB) and cyclooctadiene (COD). The dinuclear nature has been established by spectroscopic methods and molecular weight determinations.*

Addition of triethylamine to $[Rh_2Cl_2(TFB)_2(LH_2)]$ *results in the formation of* $[Rh_2(L)(TFB)_2]_2$*. This latter compound reacts with* $[Au(PPh_3)(Me_2CO)][ClO_4]$ *to yield the polynuclear species* $[Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$*.*

The ligand LH_2 *coordinates through its imidazole nitrogens to the Rh ions, whereas the thioether S-atoms are coordinating to the Au ions, as deduced from spectroscopic measurements.*

Introduction

Coordination compounds of Rh(I) with azole-type ligands have been the subject of increasing interest during the last decade [1–20]. In these compounds the azolate ligands make use of one or more nitrogen atoms affording mono- or polynuclear (homo- and heterometallic) complexes. The nuclearity is not only determined by the type of ligand: although $[Rh_2(BiIm)(COD)_2]$ is a dinuclear complex [9], the $[Rh_4(BiIm)_2(CO)_8]$ derivative prepared by carbonylation of the former presents a tetranuclear structure [10] maintaining a square-planar coordination around the rhodium atoms. Because of the fact that some azolate Rh(I) compounds have been shown to be of interest as catalyst precursors for hydroformylation reactions [14], a further study with related azole-type ligands seemed to be of interest.

Recently Reedijk *et al.* [21] have described an interesting ligand, 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane, which presents two thioether sulfur atoms along with the imidazole nitrogen donor atoms.

The present paper describes the first results of our investigation on some dinuclear and heteronuclear Rh(I) compounds with the ligand 1,6-bis(2′-benzimidazolyl)-2,5-dithiahexane.

Results and Discussion

The addition of 1,6-bis(2′-benzimidazolyl-2,5-dithiahexane (LH_2) to $[RhCl(diolefin)]_2$ (diolefin = tetrafluorobenzobarrelene (TFB) [22] or 1,5-cyclooctadiene (COD) [23]) suspended in methanol results in the formation of $[Rh_2Cl_2(diolefin)_2(LH_2)]$ complexes. These compounds were isolated as stable yellow solids. Molecular weight measurements show that they are dinuclear species in chloroform solution. The rhodium atoms are probably in a square planar arrangement where the LH_2 ligand acts as a bridge (through the $^{\diagdown}_{\diagup}$N atom) between two 'RhCl(diolefin)' units (*1a*). A similar bridge cleavage reaction has been recently observed for some bipyrazole ligands [19]. In fact, the cleavage of $[RhCl(diolefin)]_2$ complexes by monodentate nitrogen donors to form square-planar [RhCl(diolefin)(N-donor)] derivatives is a general reaction [23–28].

The perchlorate salts of the cationic dinuclear complexes $[Rh_2(diolefin)_2(LH_2)_2]^{++}$ can be prepared by addition of the ligand to dichloromethane solutions of $[Rh(diolefin)_2][ClO_4]$ complexes [29, 30].

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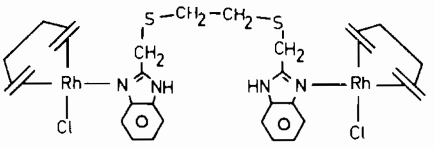
TABLE I. Analytical Results, Molecular Weights, IR Data and Yields for the Isolated Complexes.

Complexes	Found (calcd.) (%)			Mol. weights Found (calcd.)	ν(N–H) (cm^{-1})	Yields (%)
	C	H	N			
$[Rh_2Cl_2(COD)_2(LH_2)]$	47.66 (48.18)	4.98 (4.99)	6.25 (6.61)	822 (847)	3400(br)	88
$[Rh_2Cl_2(TFB)_2(LH_2)]$	46.27 (46.55)	3.06 (2.79)	5.25 (5.17)	1109 (1083)	3400(br)	84
$[Rh_2(COD)_2(LH_2)_2][ClO_4]_2$	46.95 (46.96)	4.47 (4.54)	8.10 (8.42)		3210(br)	90
$[Rh_2(TFB)_2(LH_2)_2][ClO_4]_2$	46.18 (46.02)	3.49 (3.08)	6.93 (7.15)		3200(br)	90
$[Rh_2(L)(TFB)_2]_2$	50.60 (49.81)	3.32 (2.79)	5.65 (5.55)	2103 (2024)		90
$[Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$	43.27 (43.98)	2.74 (2.93)	2.63 (2.57)			70



1a

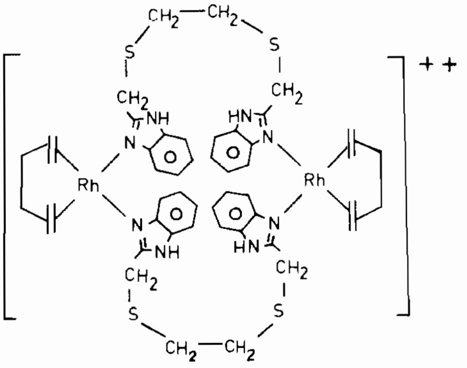
An alternative route involves the addition of the ligand to solvated species (eqn. 1):

$$[RhCl(diolefin)]_2 + 2AgClO_4 \xrightarrow{Me_2CO} 2[Rh(diolefin)(Me_2CO)_x][ClO_4] + 2\,AgCl$$

$$2[Rh(diolefin)(Me_2CO)_x][ClO_4] + 2LH_2 \rightarrow [Rh_2(diolefin)_2(LH_2)_2][ClO_4]_2 \qquad (1)$$

The dinuclearity of these complexes was established by measuring conductivities in acetone at different concentrations (10^{-3}–10^{-4} *N*). The values of A in Onsager's equation ($\Lambda_e = \Lambda_o - A\sqrt{c}$) [31] were 1133 for the tetrafluorobenzobarrelene derivative and 1087 for the cyclooctadiene derivative.

The complex $[Rh_2(TFB)_2(LH_2)_2][ClO_4]_2$ was soluble enough to obtain its ^1H NMR spectrum in $(CD_3)_2CO/(CD_3)_2SO$. Along with the resonances of the symmetrically coordinated diolefin (5.59 ppm (m, 2H) and 3.85 (m, 4H) [32], two resonances of the methylene groups of the ligand were observed at 4.31 ppm (s, 4H from $C(1)H_2$*) and 2.81 ppm (s, 4H from $C(2)H_2$*). While $C(2)H_2$ protons present values very close to those observed for the free ligand [33], it is noteworthy to point out that $C(1)H_2$ (4.31 ppm) and the aromatic protons (7.7 and 7.3 ppm), of the coordinated ligand move downfield (free ligand: 3.98 ppm ($C(1)H_2$), 7.51 and 7.15 ppm (aromatic) [33]). These data suggest that the rhodium atom is coordinated through the $\overset{\diagdown}{\underset{/}{}}N$ atom* (*1b*) [34].



1b

The addition of triethylamine to a methanol solution of $[Rh_2Cl_2(TFB)_2(LH_2)]$ leads to the elimination of the acid protons of the benzimidazole groups with formation of $[Rh_2(L)(TFB)_2]_n$. The complex was isolated as a light yellow solid. The experimental molecular weight measurements indicate that n has a value of 2.

All compounds listed in Table I analysed satisfactorily. Each imidazolyl group of the ligand could act as monodentate in $[Rh_2Cl_2(diolefin)_2(LH_2)]$ or $[Rh_2(diolefin)_2(LH_2)_2][ClO_4]_2$ complexes, or as exobidentate in $[Rh_2(L)(TFB)_2]_2$ (*1c*).

In order to use all the potential coordination atoms of the ligand, we have studied the reaction of $[Rh_2(L)(TFB)_2]_2$ with $[AuCl(PPh_3)]$ and $AgClO_4$ ($[Au(PPh_3)(Me_2CO)][ClO_4]$) (eqn. 2):

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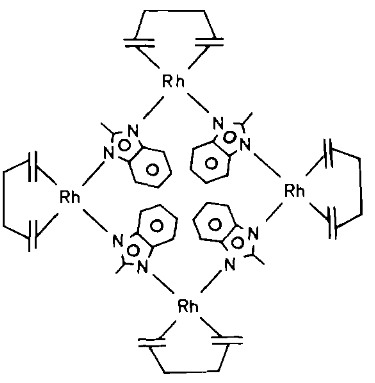
*The atomic numbering is as follows: $(C_7H_5N_2\text{-}C(1)H_2\text{-}SC(2)H_2\text{-})_2$.



1c

$$\tfrac{1}{2}[Rh_2(L)(TFB)_2]_2 + 2[AuCl(PPh_3)] + 2\,AgClO_4$$

$$\xrightarrow{Me_2CO} 1/n\ [Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n} + {} + 2AgCl \qquad (2)$$

Elemental analyses support the proposed formula. In this complex the ligand most likely binds to gold *via* the thioether sulfur atoms and to rhodium *via* the imidazole nitrogen atoms. Conductivity studies at different concentrations afford a value of A in Onsager's equation of 770. This value suggests that the parent structure has changed to lower nuclearity ($n < 2$). Changes in nuclearity by simple reactions have been previously observed in the $[Rh_2(BiIm)(COD)_2]$ and $[Rh_4(BiIm)_2(CO)_8]$ complexes [9, 10].

In all diolefin complexes described in this paper the ligand (LH_2 or L) most likely binds to rhodium by nitrogen atoms (see *1a–c*). Nevertheless weak coordination by a fifth ligand (such as thioether) cannot be totally excluded. In fact, we have recently found that the square-planar $[Rh(NBD)_2]^+$ cation reacts with SEt_2 with formation of $[Rh(NBD)_2(SEt_2)]^+$ where the observed Rh–S distance is rather long (2.50 Å) [35].

Bubbling carbon monoxide through chloroform solutions of $[Rh_2(L)(diolefin)_2]_2$ and $[Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$ suggests the formation of $[Rh_2(L)(CO)_4]_n$ (ν(CO): 2080, 2010 cm^{-1}) and $[Rh_2(L)(CO)_4\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$ (ν(CO): 2090, 2030 cm^{-1}). When a stoichiometric amount of triphenylphosphine was added, the related $[Rh_2(L)(CO)_2(PPh_3)_2]_n$ (ν(CO): 1985 cm^{-1}) and $[Rh_2(L)(CO)_2(PPh_3)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$ (ν(CO): 1990 cm^{-1}) derivatives seem to be formed. Unfortunately, the yellow solids obtained from these solutions are not analytically pure, although the ν(CO) bands of the solids still suggest the proposed formulations.

Experimental

Reactions were carried out at room temperature under air. Solvents were distilled before use. C, H, N analyses were carried out with a Perkin-Elmer 240 microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls. Molecular weights were measured in $CHCl_3$ with a Perkin-Elmer 115 osmometer. Conductivities were measured in acetone solutions with a Phillips 9501/01 conductimeter. NMR spectra at 100 MHz were recorded on a JEOL PS-100 spectrometer.

Preparation of the Compounds of the $[Rh_2Cl_2(diolefin)_2(LH_2)]$ Type

To a suspension of $[RhCl(diolefin)]_2$ (diolefin = TFB or COD) in methanol, a stoichiometric amount of LH_2 in the same solvent was added. After stirring for a few minutes a yellow solution was obtained. This solution was filtered to remove any remaining solid and the filtrate concentrated to dryness under reduced pressure. The yellow residue was recrystallized from dichloromethane/diethylether to give the $[Rh_2Cl_2(diolefin)_2(LH_2)]$ complexes.

Preparation of the Compounds of the $[Rh_2(diolefin)_2(LH_2)_2][ClO_4]_2$ Type

The compounds were made by the two routes described below:

i) To a solution of $[Rh(diolefin)_2][ClO_4]$ in dichloromethane, a stoichiometric amount of LH_2 in the same solvent was added. After a few minutes a yellow precipitate began to form. The resulting suspension was stirred for 15 minutes. The precipitate was filtered off and recrystallized from acetone/diethylether to give the analytically pure $[Rh_2(diolefin)_2(LH_2)_2][ClO_4]_2$ complexes.

ii) To a suspension of $[RhCl(diolefin)]_2$ in acetone, a stoichiometric amount of silver perchlorate in the same solvent was added. The resulting suspension was stirred for 30 minutes and then filtered through Kieselguhr. An acetone suspension containing a stoichiometric amount of LH_2 was added to the light yellow filtrate. After some minutes the yellow solution formed was concentrated to dryness under reduced pressure. The yellow residue was recrystallized from acetone/diethylether to give the formulated complexes.

Preparation of $[Rh_2(L)(TFB)_2]_2$

When triethylamine (2:1 ratio) was slowly added to a methanolic solution of $[Rh_2Cl_2(TFB)_2(LH_2)]$, prepared as above, a light yellow precipitate was formed instantaneously. The resulting suspension was stirred for 1 hour and then the precipitate filtered off. The light yellow solid separated was washed with diethylether and air-dried.

Preparation of $[Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n$-$[ClO_4]_{2n}$

To a suspension of $[AuCl(PPh_3)]$ in acetone a stoichiometric amount of silver perchlorate in the same solvent was added. The resulting suspension was stirred for 15 minutes and then filtered through Kieselguhr. The colourless filtrate was recovered over a suspension of $[Rh_2(L)(TFB)_2]_2$ in acetone. The solid dissolved and the resulting yellow solution was stirred for 30 minutes. The solution was then concentrated to dryness under reduced pressure and the residue recrystallized from dichloromethane/hexane to give a pure sample analysing as $[Rh_2(L)(TFB)_2\{Au(PPh_3)\}_2]_n[ClO_4]_{2n}$.

Carbonylation Reactions

Carbon monoxide was bubbled through chloroform solutions at room temperature and 1 atmosphere of pressure. No significant colour changes were observed in the solutions, but the IR spectra show the instantaneous formation of carbonyl derivatives.

Conclusions

The results described in this paper show that 1,6-bis(2′-benzimidazolyl)2,5-dithiahexane is able to coordinate to Rh(I) in a versatile manner. The S atoms of the ligand seem to coordinate to Au in the heteronuclear compounds.

The catalytic properties of these and related ligands and Rh compounds are under investigation.

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