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Preliminary communication

CATIONIC RHODIUM(I) COMPLEXES WITH NORBORNADIENE AND NITROGEN DONORS

R. USÓN*, L.A. ORO, J.A. CUCHI and M.A. GARRALDA
Department of Inorganic Chemistry, University of Zaragoza (Spain)
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Summary

A general method is described for the preparation of cationic rhodium(I) complexes with norbornadiene (NBD) and both monodentate and chelate nitrogen donor ligands, and some substitution reactions of the complexes are discussed.

Treatment of $[(NBD)RhCl]_2$ with a stoichiometric amount of $AgClO_4$ (in dichloromethane solution) and norbornadiene (NBD) in excess leads to the formation of a solution of bis(norbornadiene)rhodium(I) perchlorate (eq. 1).

$$[(NBD)RhCl]_2 + 2\,AgClO_4 + 2\,(NBD) \longrightarrow 2\,AgCl + 2\,[(NBD)_2Rh]ClO_4 \quad (1)$$

After the precipitated AgCl is filtered off, the filtrate can be used as precursor [1—3] for the preparation of a series of complexes of the $[(NBD)RhL_2]ClO_4$ type (where L = a monodentate N donor; or $\frac{1}{2}$ (L—L) = a N,N-donor chelate). Thus, the addition of a stoichiometric amount of the nitrogen-donor ligand (in dichloromethane solution) resulted in the replacement of one mol of (NBD) according to eq. 2.

$$[(NBD)_2Rh]^+ + 2\,L(\text{or } L\text{—}L) \longrightarrow (NBD) + [(NBD)RhL_2]^+ \quad (2)$$

The product precipitated spontaneously (mainly in the case of the chelate ligands) or on addition of diethyl ether or n-pentane. Replacement of the second mol of (NBD) could not be accomplished, even by use of an excess of the ligand L or (L—L).

The perchlorate salts of the cationic complexes, prepared according to eq. 2, have been isolated for L = quinoline, isoquinoline, pyridine or 2-ethylpyridine, or (L—L) = *N,N,N',N'*-tetramethylethylenediamine, 1,2-diphenylethylenediamine, 2,2'-bipyridine or 1,10-phenantroline. The first six products are yellow

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*To whom correspondence should be addressed.

microcrystalline complexes, while the last two are orange-red crystals. All give satisfactory C, H and N analyses. In acetone their conductivities are those expected for 1:1 electrolytes ($\Lambda_M = 120$—140 ohm^{-1} cm^2 mol^{-1} in $\sim 10^{-4}M$ solution). Their melting or decomposition points are above 140°C. They are air stable in daylight at room temperature but some of them decompose explosively on heating.

Some reactions of the new complexes have been studied:

(a) The monodentate ligands can be replaced by any of the chelate ligands mentioned above.

$$[(NBD)RhL_2]^+ + L{-}L \longrightarrow [(NBD)Rh(L{-}L)]^+ + 2\ L \qquad (3)$$

Thus eq. 3 can be readily displaced to the right by using an excess of (L—L). Moreover, the aliphatic diamines are replaced by 2,2′-bipyridine and 1,10-phenantroline (eq. 4).

$$[(NBD)Rh(diamine)]^+ + phen \longrightarrow [(NBD)Rh(phen)]^+ + (diamine) \qquad (4)$$

This reaction cannot be reversed even by use of an excess of the diamine.

(b) All the complexes react with triphenylphosphine and the replacement of the monodentate N-donor ligands can take place stepwise according to eq. 5.

$$[(NBD)RhL_2]^+ \xrightarrow{PPh_3} [(NBD)RhLPPh_3]^+ \xrightarrow{PPh_3} [(NBD)Rh(PPh_3)_2]^+ \qquad (5)$$

Four mixed cationic complexes have been isolated in form of the perchlorate salts $[(NBD)RhLPPh_3]ClO_4$ (L = quinoline, isoquinoline, pyridine or ethylpyridine); the complex $[(NBD)Rh(PPh_3)_2]ClO_4$ [4] has finally been obtained. All these were characterized by elemental analyses (C,H,N) and their conductivities were determined.

The complexes with (L—L) = 2,2′-bipyridine or 1,10-phenantroline react with triphenylphosphine to give mixtures of products which could not be resolved. The analytical results fall between those for the starting compounds and those for the expected pentacoordinate species $[(NBD)Rh(L{-}L)PPh_3]ClO_4$.

(c) Dichloromethane solutions or suspensions of all the cationic complexes undergo carbonylation with CO at ordinary pressure with replacement of the diolefin. The carbonylation of the complexes containing monodentate ligands or aliphatic diamine leads to dicarbonyl derivatives according to eq. 6.

$$[(NBD)RhL_2]^+ + 2\ CO \longrightarrow (NBD) + [(CO)_2RhL_2]^+ \qquad (6)$$

(L = monoamine or phosphine; L_2 = aliphatic diamine). However tricarbonyl derivatives are obtained when L_2 = 2,2′-bipyridine or 1,10-phenantroline [5] (eq. 7)

$$[(NBD)Rh(bipy)]^+ + 3\ CO \longrightarrow (NBD) + [(CO)_3Rh(bipy)]^+ \qquad (7)$$

(d) Some of the complexes catalyse the hydrogenation of cyclic or terminal olefin and a systematic study of this catalysis is in progress.

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