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BINUCLEAR RHODIUM(I) COMPLEXES. SYNTHESIS OF $[Rh(COD)]_2L(OAc)_2$ WHERE L IS THE NEW 22-MEMBERED MACROMONOCYCLE 1,4,7,12,15,18-HEXAAZACYCLODOCOSANE

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Summary

Reaction of $[Rh(COD)(OAc)]_2$ with the new 22-membered macromonocyclic hexaamine 1,4,7,12,15,18-hexaazacyclodocosane (L) yields the binuclear species $[Rh(COD)]_2L(OAc)_2$. Comparison with a mononuclear model complex formed from diethylethylenediamine (DEEN) indicates that the binuclear compound contains two Rh(COD) units, each bound to two ligand nitrogens. The synthesis, spectra, and properties of the complexes $[Rh(COD)]_2L(OAc)_2$ and Rh(COD)(DEEN)(OAc) are reported.

There is considerable interest in the synthesis of new binuclear transition metal complexes in which ligand frameworks are used to control the intermetal separations and maintain structural integrity [1—4]. These complexes are expected to exhibit unique reactivity as a result of cooperative interactions between functionally independent metals that are not strongly interacting. Such bimetallic species might be particularly useful at effecting transformations involving (i) the activation of single substrates via unusual bridging modes between the metals (ii) simultaneous activation of two substrates on adjacent centers and (iii) multielectron redox processes.

Our approach to discrete binuclear complexes of this type employs macrocyclic ligands to position the metals close together. For this reason, we have recently developed a versatile synthetic route to new macromonocyclic hexaamines of varying ring size [5] and are examining their ability to form bi- and polynuclear compounds with a variety of transition metals. We report here the synthesis of a binuclear Rh^I complex, $[Rh(COD)]_2L(OAc)_2$, I, of one such macrocycle, 1,4,7,12,15,18-hexaazacyclodocosane (L). Complexes having two $Rh(CO)_2$ units bound to tetraaza macrocycles have been previously synthesized [6,7] but the carbonyls are not readily substituted, even in the presence of excess phosphine, and the Rh centers do not undergo oxidative additions with alkyl halides [6]. We therefore chose cyclooctadiene (COD) as a ligand, since it would stabilize low-valent Rh^I in the presence of nitrogen donors of the macrocycle and could be removed by mild hydrogenation [8] to generate reactive bimetallic sites.

Slow addition of L to an orange solution containing a 50% excess of $[Rh(COD)(OAc)_2]$ [9] in dry benzene under argon resulted in the precipitation of a light yellow, air-sensitive powder. The powder was isolated by filtration, washed thoroughly with dry benzene, and dried under vacuum (70% yield). TLC on alumina with CH_3OH gave only one spot (R_f of ca. 0.6). Neither $[Rh(COD)(OAc)]_2$ nor L were mobile under these conditions and were not found to be present in the product. Analysis indicated the presence of the binuclear complexes as well as solvate molecules of acetic acid and benzene (Found: Rh, 21.66; C, 50.64; H, 8.05; N, 9.04. Calcd. for $Rh_2(COD)_2L(OAc)_2 \cdot HOAc \cdot 1/3C_6H_6$: Rh, 21.87; C, 51.06; H, 7.93; N, 8.93%). Using diethylethylenediamine (DEEN), the corresponding mononuclear complex, Rh(COD)(DEEN)(OAc), II, was prepared as a yellow solid in 66% yield by a similar procedure (Found: C, 48.34; H, 8.20; N, 6.34. Calcd. for $Rh(COD)(DEEN)(OAc) \cdot HOAc$: C, 48.43; H, 7.90; N, 6.27%). These compounds were further characterized by IR, NMR, and absorption spectroscopy and by conductivity measurements.

Both ^1H and ^{13}C NMR spectra ($CDCl_3$, δ relative to i-TMS) for the complexes were broad and poorly resolved, but clearly indicated the presence of the ligands, COD, and acetate. For example, the ^1H spectrum for I exhibited a broad ligand absorption centered at 3.00 ppm (H's on carbons adjacent to ring nitrogens) with a singlet superimposed upon it at 2.38 ppm (COD alkyl H's), and another singlet at 2.00 ppm (acetate methyl H's). The ^{13}C spectra were very broadened, particularly in the alkyl regions. The COD resonances were found at 79 ppm (olefinic) and 31 ppm (aliphatic), in good agreement with the values reported for $[Rh(COD)Cl]_2$ (78.5 and 30.9 ppm, respectively) [10]. The acetate methyl resonance appeared as a sharp singlet at 28 ppm, but the carbonyl peak (ca. 180 ppm) was very weak. The ligand alkyl carbons bound to the nitrogens gave a broad band at about 49 ppm, in the same position as was found for the free ligand.

The IR spectra (KBr pellets) for both compounds were quite similar. Ligand amine (3250—3075 cm^{-1}) and alkyl (2960—2840 cm^{-1}) bands were observed, along with two strong bands (1585 and ca. 1400 cm^{-1}) from the acetate. For the mononuclear complex II, a single amine stretch was observed at 3075 cm^{-1}. However, for the binuclear complex I, two amine stretches, at 3250 and 3100 cm^{-1}, were assigned to free and bound amines, respectively. The higher frequency acetate band was found at 1585 cm^{-1} in both complexes. For II the lower frequency band was found at 1415 cm^{-1}, indicative of ionic acetate (cf. NaOAc, ν = 1414 cm^{-1}) [11]. In the binuclear complex, the corresponding band was found at a lower frequency (1395 cm^{-1}).

The visible absorption spectra of the compounds (CH_2Cl_2 solution) are shown in Fig. 1. The absorptions at 370 and 380 nm are assigned to Rh—COD charge transfer transitions [12]. The extinction coefficient of a single Rh(COD

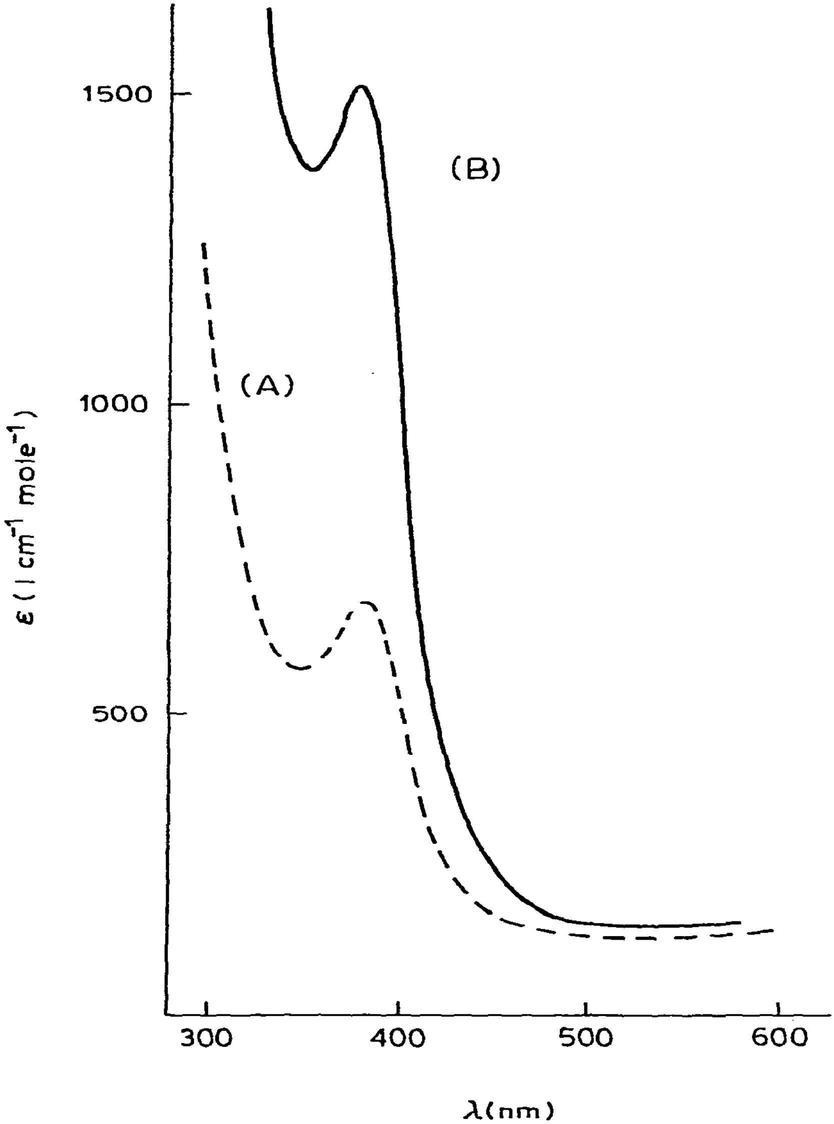

Fig. 1. Visible absorption spectra of (A) Rh(DEEN)(COD)(OAc), (- - - -) and (B) $[Rh(COD)]_2L(AOc)_2$, (——).

chromophore is about 625 l cm^{-1} mol^{-1}, based on that observed for the mononuclear complex II. For the binuclear complex I, the observed extinction coefficient was roughly twice that value, indicating the presence of two such chromophores. Neither complex exhibited a band at 420 nm which was observed in the starting rhodium dimer due to rhodium—acetate charge transfer.

Both compounds I and II were found to be 1:1 electrolytes in 10^{-3} *M* CH_3NO_2 solutions (Λ: I, 73; II, 69).

Based on these results, structures for these complexes are proposed in Fig. 2. In the case of I, several isomers can be envisioned; however, only one

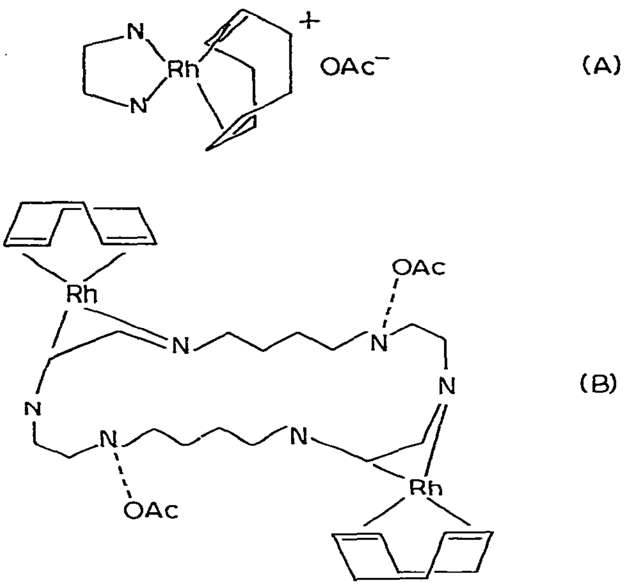

Fig. 2. Proposed structures for (A) Rh(DEEN)(COD)(OAc) and (B) [Rh(COD)]$_2$L(OAc)$_2$. H's and DEEN ethyls are not shown.

such possibility is depicted here. The Rh coordination geometry is most likely square-planar, as has been reported previously for complexes with amine macrocycles [6]. Five-coordinate Rh^{I} complexes [13] in which a third nitrogen of the ring is interacting with the metal are also possible but do not appear likely based on comparison of the IR and absorption data for I and II. The absence of low energy absorptions in the electronic spectrum of I rules out the existence of direct Rh—Rh interactions [14]. The integrity of the Rh(COD) units are clearly demonstrated by the absorption data. For II, both the IR and conductivity results indicate that the acetate is ionic; for I, these results suggest that the acetates are interacting with the complex. The absence of a Rh—OAc absorption in the visible spectrum leaves the ligand free amines as likely candidates for this interaction. We have structurally characterized such an interaction between perchlorate anions and protonated amines in a binuclear Cu complex of L [15] and are currently trying to grow crystals suitable for obtaining an X-ray structure of I.

Additionally, the reaction of the 24-membered analog of L, 1,4,7,13,16,19-hexaazacyclotetracosane, with [Rh(COD)(OAc)]$_2$ has been carried out. Preliminary results indicate that the product is not a simple analog of I and may, in fact, be trinuclear.

Finally, mild hydrogenation (1 atm, 25°C, 15 min) of I produced a highly reactive intermediate that could be trapped with phosphines (e.g. bis(1,2-diphenylphosphino)ethane) to give a product devoid of COD (no 370 nm visible absorption) but containing the phosphine and L (by ^{1}H NMR). We are now exploring this method to synthesize other binuclear Rh complexes possessing a single bridge such as bis(diphenylphosphino)methane (DPM) between the metals. These complexes would have a Rh$_2$(DPM) fragment girdled by the macrocycle in a manner resembling the A-frames [16]. The reactivity of such binuclear compounds with small molecules may lead to new and unusual catalytic chemistry.

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