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Preliminary communication

PREPARATION AND REACTIONS OF CHLORO-TRIS(2,6-XYLYL ISOCYANIDE)-RHODIUM

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Summary

Reaction of $[Rh(COD)Cl]_2$ with 2,6-xylyl isocyanide at room temperature gave a neutral complex, $Rh(C_9H_9N)_3Cl$, $\underline{1}$. The reactions of $\underline{1}$ with bases, olefins, and alkyl halides are described.

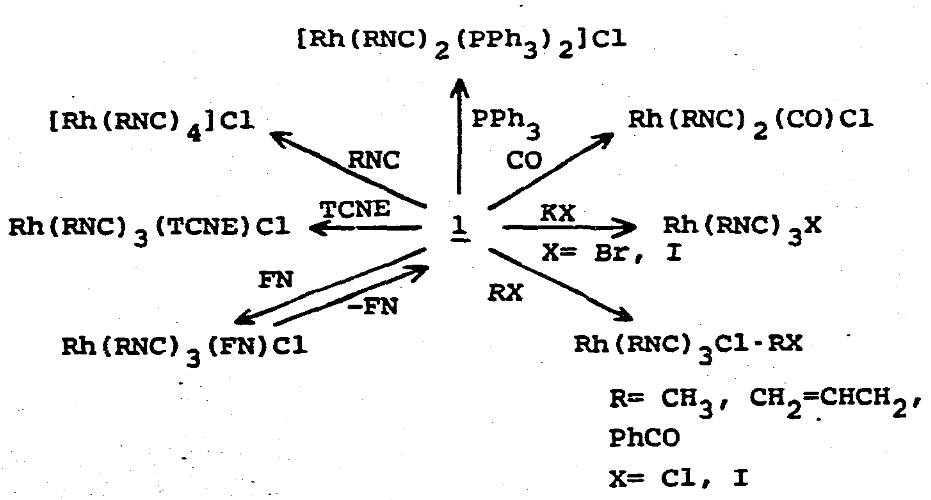
It has been reported that isocyanides react with $RhCl_3 \cdot 3H_2O$ or $[Rh(CO)_2Cl]_2$ to give cationic complexes, $[Rh(RNC)_4]Cl$.[1] However, no neutral isocyanide complexes of a type similar to $Rh(PPh_3)_3Cl$ have been described. We report here the preparation of $Rh(RNC)_3Cl$ complexes by the stoichiometric reactions of $[Rh(COD)Cl]_2$ with 2,6-xylyl isocyanide.

When $[Rh(COD)Cl]_2$ was treated with 2,6-xylyl isocyanide in 1:6 molar ratio, followed by chromatography on alumina, yellow crystalline $Rh(C_9H_9N)_3Cl$, $\underline{1}$, was isolated (84-90%, mp 178-180° (dec), ir(KBr): 2145 and 2105cm^{-1}, m.wt.(VPO in benzene): 561(calcd 532)). The nmr spectrum of $\underline{1}$ in $CDCl_3$ showed two methyl resonances at δ 2.40(s) and 2.50(s, ppm in 1:2 intensity ratio, showing that $\underline{1}$ has a square planar configuration, compared with that of $Rh(PPh_3)_3Cl$.[2] The electronic spectrum showed four absorption bands at 444(ε 250), 403(ε 3200), 333(ε 39700), and 235 (ε 68000) nm, but no absorption bands beyond 500 nm, suggesting that association[3] of rhodium complexes through formation of metal-metal bonds, which has been observed in cationic isocyanide complexes of type $[Rh(RNC)_4]^+$, does not occur in the neutral complex.

Compound 1 was converted to the bromide and iodide derivatives by metathetic reaction with potassium bromide or iodide. Reaction of 1 with 2,6-xylyl isocyanide gave the known cationic complex $[Rh(C_9H_9N)_4]Cl$.[4] Reactions with carbon monoxide and triphenylphosphine produced $Rh(C_9H_9N)_2(CO)Cl$ and $[Rh(C_9H_9N)_2(PPh_3)_2]Cl$, respectively. Reaction of 1 with tetracyanoethylene(TCNE) occurred readily to afford a 1:1 adduct, $Rh(C_9H_9N)_3(TCNE)Cl$. The nmr spectrum of this adduct in $CDCl_3$ showed only one singlet at δ 2.55 ppm due to the methyl groups, but the nmr spectra of the corresponding bromide and iodide TCNE adducts showed two kind of methyl resonances. The infrared spectra of the three TCNE complexes showed similar patterns. Thus, the nmr behavior of the chloride complex can be explained by an accidental degeneracy of the two kinds of methyl proton resonances. Various structures for these complexes may be considered. We tentatively favor a trigonal bipyramid with TCNE and two RNC ligands occupying the equatorial positions, since a configuration of this kind is well established for the TCNE adducts of rhodium[5] and iridium.[6] No reaction occurred between 1 and fumaronitrile(FN) at room temperature but at 90° $Rh(C_9H_9N)_3(FN)Cl$ was formed. This compound eliminated coordinated fumaronitrile to regenerate $Rh(C_9H_9N)_3Cl$ when it was heated in the solid state at 80° under reduced pressure.

Reactions with methyl iodide, allyl chloride, or benzoyl chloride proceeded readily with oxidative addition to give the corresponding $Rh(C_9H_9N)_3Cl \cdot RX$ (R= CH_3, $CH_2{=}CHCH_2$, or PhCO; X= Cl or I). In the nmr spectra of these complexes, two resonances due to o-methyl groups were observed, suggesting a tetragonal bipyramidal structure. The ν(NC) bands of these products are higher than that of the starting complex by ca $30 cm^{-1}$, reflecting the oxidation state of the metal.

Compound 1 did not react with phenylethylaldehyde even at 155°. In contrast, $Rh(PPh_3)_3Cl$ reacts with aldehydes at room temperature to give $Rh(PPh_3)_2(CO)Cl$ and the corresponding paraffins.[7] It is well known that $Rh(PPh_3)_3Cl$ catalyzes the hydrogenation of olefins at room temperature. However, the compound 1 was found to be inactive under these same conditions. The observed low reactivity of 1, as contrasted with the high reactivity of $Rh(PPh_3)_3Cl$, probably is a result of the absence of dissociation of an isocyanide ligand.



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