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Preliminary communication

ISONITRILE COMPLEXES DERIVED FROM THE NUCLEOPHILIC ATTACK OF PRIMARY AMINES ON THE DITHIOMETHYL ESTER COMPLEX, $RuI(CO)(PPh_3)_2(CS_2Me)$

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Summary

The bidentate dithiomethyl ester complex, $RuI(CO)(PPh_3)_2(CS_2Me)$ reacts with primary amines affording a series of novel dimeric isonitrile complexes, $[RuI(CO)(CNR)(PPh_3)_2SH]_2$.

In a previous communication [1], the formation of $RuI(CO)(PPh_3)_2(CS_2M$ and its reaction with hydroiodic acid to give the thiocarbonyl complex, $RuI_2(CO)(CS)(PPh_3)_2$, was reported. Recently, it has been shown that transition-metal thiocarbonyl complexes are susceptible to nucleophilic attack by primary amines which results in the formation of isonitrile complexes [2,3]. This prompts us to report our findings on the reaction of primary amines with the dithiomethyl ester complex $RuI(CO)(PPh_3)_2(CS_2Me)$ to give a series of dimeric isonitrile complexes.

A series of primary amines, RNH_2 (R = Me, n-Pr, i-Pr, n-Bu, s-Bu and Bz) was found to react with $RuI(CO)(PPh_3)_2(CS_2Me)$ dissolved in refluxing benzene to produce a yellow solution after three hours. From this solution yellow crystals of $[RuI(CO)(CNR)(PPh_3)_2SH]_2$ were obtained in 70% yield upon the addition of hexane. Molecular weights obtained in $CHCl_3$ were in the range 1125—1367.

The IR spectra (Table 1) of these compounds contain $\nu(CO)$ in the region 1974—1954 cm^{-1}, which is characteristic of ruthenium(II) complexes. The presence of only one carbonyl stretching frequency indicates that the carbonyl are *trans* to each other. The IR spectra include only $\nu(CN)$ absorption in the region 2196–2168 cm^{-1}, which also implies both isonitriles are coordinated in a *trans* fashion. The low solubility of these compounds in deuterated solvent precluded the possibility of NMR studies on the instruments available.

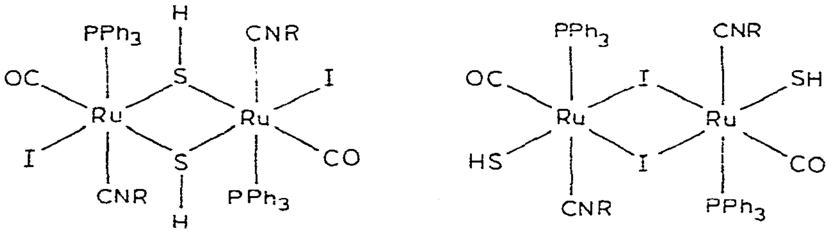
These complexes are believed to contain either iodide or thiol bridging ligands (Fig. 1). IR data cannot distinguish between the possibilities A and B.

TABLE 1

INFRARED DATA FOR ISONITRILE COMPLEXES[a] $[RuI(CO)(CNR)(PPh_3)SH]_2$

R group	ν(CO) (cm^{-1})vs[b]	ν(CN) (cm^{-1})s[b]
Methyl	1971	2196
n-Propyl	1974	2180
Isopropyl	1972	2176
n-Butyl	1968	2173
sec-Butyl	1972	2172
Benzyl	1954	2168

[a] All spectra were obtained as Nujol mulls and satisfactory analyses were obtained for all compounds.
[b] s = strong, vs = very strong.

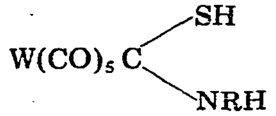


(A) (B)

Fig. 1. Proposed structures of $[RuI(CO)(CNR)(PPh_3)SH]_2$.

From previously reported complexes containing terminal SH groups, the SH stretching frequency could not be identified [4—6]. This is probably due to an initially weak absorption which is shifted and broadened by hydrogen bonding. Complexes containing bridging SH ligands have been reported to exhibit weak to medium SH absorption in the region 2571—2481 cm^{-1} [7,8]. Although the absence of an SH absorption in the IR spectrum is consistent with the iodide bridging structure B, it is not conclusive evidence for this structure.

The proposed mechanism of reaction is similar to that of Angelici et al. [2], in which the thiocarbonyl carbon of $W(CO)_5(CS)$ undergoes nucleophilic attack by primary amines to give the carbene complex,



$W(CO)_5C(SH)(NRH)$

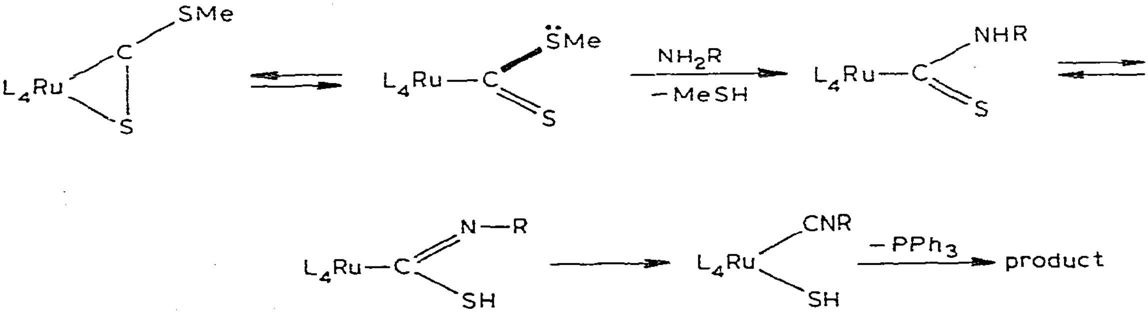


Fig. 2. Proposed mechanism for the formation of $[RuI(CO)(CNR)(PPh_3)SH]_2$ ($L_4 = I(CO)(PPh_3)_2$).

From this, H_2S is rapidly lost yielding $W(CO)_5(CNR)$. Our mechanism assumes an equilibrium between the bidentate and monodentate dithiomethyl ester ligand (Fig. 2), followed by nucleophilic attack at carbon with the simultaneous release of odorous MeSH to give a monodentate thiocarboxyamido intermediate. Proton transfer to sulphur and migration of the thiol group result in the formation of the isonitrile ligand. The final step of the reaction involves loss of triphenylphosphine and dimerization to give the isolated product.

Further work is continuing on the structure and reactivity of dithiomethyl ester complexes, in particular their general reactivity towards nucleophilic attack.

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