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Preliminary communication

Sulfurdiimine and carbodiimine compounds of rhodium and platinum

J. KUYPER, K. VRIEZE and A. OSKAM
Anorganisch Chemisch Laboratorium, Nieuwe Achtergracht 123, Amsterdam, The Netherlands

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SUMMARY

The preparations and properties of the first sulfurdiimine complexes and of some carbodiimine complexes of rhodium and platinum are reported.

Research into the coordinating properties of allenes directed our attention to the study of metal compounds of sulfurdiimines (–N=S=N–) and carbodiimines, which may coordinate either via the double bonds or via the lone pairs of N and S. The close proximity of the double bonds and the lone pairs may, furthermore, provide a low energy pathway for intra- and intermolecular rearrangements of the metal atom along the ligand system.

We describe below the preparation and properties of the first sulfurdiimine complexes ever reported, and also those of some carbodiimine complexes.

Sulfurdiimine compounds

By treating (ethylene)platinum dichloride dimer or rhodium carbonyl chloride dimer with di-t-butylsulfurdiimine (DBSD) monomeric (DBSD)Pt(C_2H_4)Cl_2 and (DBSD)Rh$(CO)_2$Cl were formed. These represent the first reported sulfurdiimine complexes.

NMR measurements on the Pt-complex showed that at –60° (Fig. 1) in the DBSD region, three signals occur in the ratio 5/2/5, while in the ethylene region two olefin proton signals occur in the ratio 5/1. At higher temperatures the central signal of the DBSD absorptions remains sharp, whereas the two outer high intensity signals coalesce at the weighted mean. The low intensity ethylene signal, which in intensity correlates with the central low intensity DBSD signal, showed an intermolecular ethylene exchange even at relatively low temperatures, as indicated by the disappearance of the ^{195}Pt satellites. This was not observed for the high intensity ethylene signal.

Kinetic measurements using the two outer DBSD absorptions showed that for solutions of the pure (DBSD)Pt(C_2H_4)Cl_2 in $CFCl_3$ the reciprocal of the liftime, τ, is

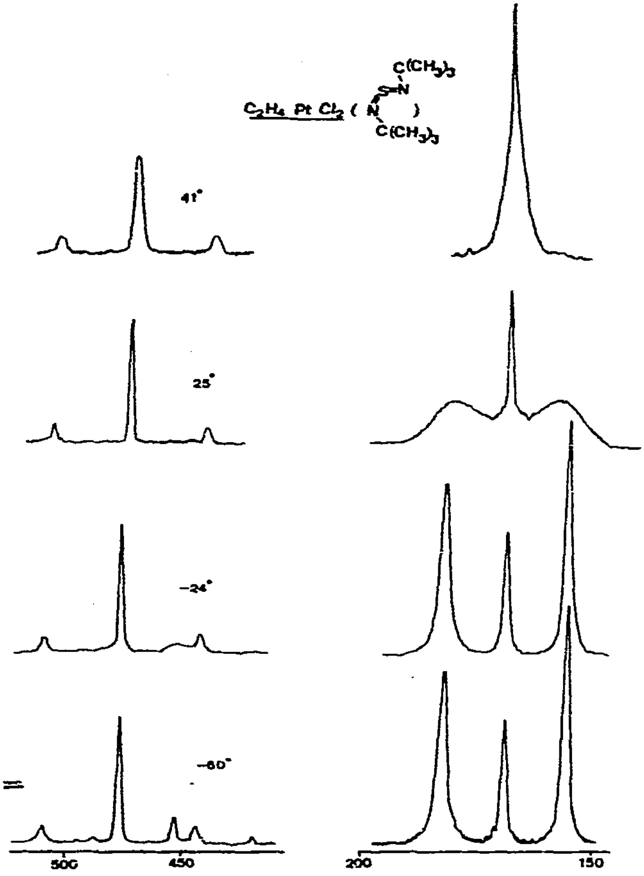

Fig. 1. PMR spectra of $(DBSD)Pt(C_2H_4)Cl_2$ in fluorochloroform at various temperatures.

independent of the concentration. In the presence of free ligand DBSD, τ^{-1} is proportional to the ligand concentration, while independent of the concentration of the compound. Noteworthy is the fact that the excess of DBSD exchanged only with the ligand responsible for the outer two absorptions. No exchange was observed for the central peak, which remained sharp and did not decrease in intensity even after several hours over a temperature range between −90° and +65°. The above clearly shows that in solution there are two isomers in the ratio 5/1 (in $CFCl_3$, $CHCl_3$, CH_2Cl_2). Both isomers contain DBSD, as shown by the observation that the reaction of $(DBSD)Pt(C_2H_4)Cl_2$ with triphenylphosphine afforded $(PPh_3)_2PtCl_2,C_2H_4$ and in quantitative yield DBSD. A single crystal X-ray structure[6] shows that the DBSD is N-bonded to the metal atom; this is probably the more abundant isomer. The plane of the DBSD molecule, which is *trans* to C_2H_4, is perpendicular to the plane of the $(C_2H_4)PtCl_2$ entity with N=S=N and Pt–N=S angles of 112° and 105° respectively. The Pt–S distance is 2.97 Å which is relatively short and might indicate a small interaction. The t-butyl groups are *trans* to each other, as in the free ligand.

The less abundant isomer, which causes the single sharp DBSD peak at 1.69 ppm (δ), probably contains the DBSD sulfur-bonded to the metal. In the crystal structure no evidence was found for this isomer and possibly the two forms crystallise out separately.

From the NMR kinetic data it is concluded that in the case of the more abundant isomer both intramolecular and intermolecular exchanges of the DBSD ligand occur, while the less abundant isomer does not enter these reactions. Very similar behaviour was found for $(DBSD)Rh(CO)_2Cl$.

A study of the sulfurdiimines themselves, which have been very little studied[7,8], showed that at low temperature (in $CFCl_3$ and $CHCl_3$) for both di-t-butylsulfurdiimine and dimethylsulfurdiimine there are two NMR absorptions in the ratio 1/1; the methyl peaks of the latter compound being split into quartets due to a long range coupling of approximately 1.4 cps. It is clear that in both cases there is only one isomer at low temperatures, namely the *cis,trans* isomer analogous to the conformation in the platinum compound. At higher temperatures the signals of the butyl compound (1.35 and 1.45 ppm from TMS) coalesce with no evidence of intensity changes (1.40 ppm), which indicates the following reaction shown in Fig. 2.

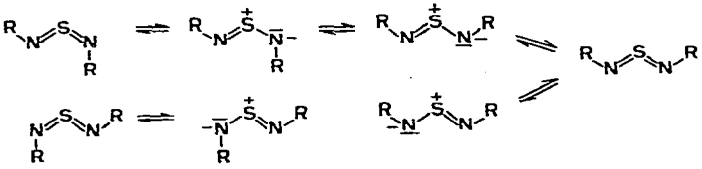

Fig. 2.

The interconversion process, which has as activation parameters $\Delta E = 13$ kcal·mole^{-1} and $A = 10^{13}$ sec^{-1}, probably proceeds via the *trans,trans* isomer as an intermediate, the *cis,cis* isomer being sterically the less favourable.

The methyl signals (two quartets at 3.67 and 3.55 ppm) of the dimethylsulfurdiimine change in intensity with increase in temperature, while simultaneously broadening and finally coalescing to one signal (3.59 ppm) occurred. Clearly the *trans,trans* isomer possesses an appreciable lifetime at higher temperatures, and the *cis,cis* isomer may possibly behave similarly.

By means of ^{13}C NMR it has been shown unequivocally that two isomers occur at low temperature in the case of bis(3,5-dimethylphenyl)sulfurdiimine, which interconvert at higher temperatures.

Diimine compounds

In addition to the sulfurdiimine compounds, the carbodiimine compounds $LPt(C_2H_4)Cl_2$, $LPt(TMA)Cl_2$ and $LRh(CO)_2Cl$ were prepared in which L = di-t-butylcarbodiimine, and diisopropylcarbodiimine. Both intra- and inter-molecular exchange of the carbodiimine occurs in these complexes also.

Details of these, and many other new sulfur- and carbodiimine compounds of the later transition metals, will be published elsewhere.

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