UNIVERSITA' DI MESSINA
FACOLTA' DI SCIENZE

Dipartimento di Chimica Inorganica, Analititca
e Struttura Molecolare

Società Chimica Italiana
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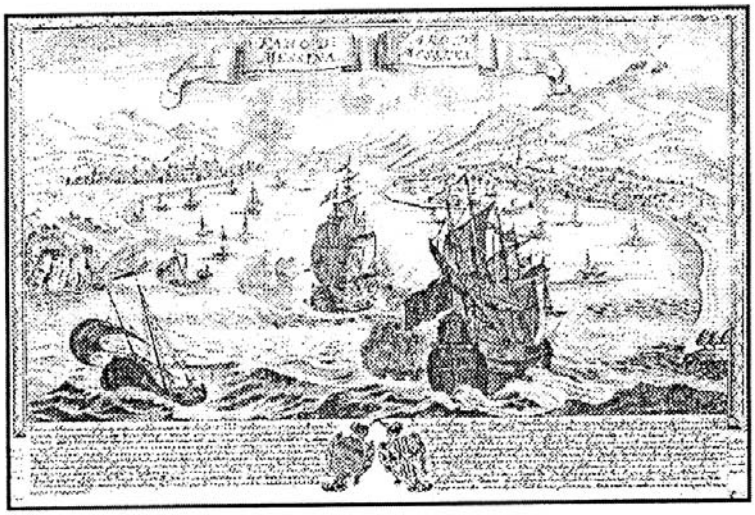
Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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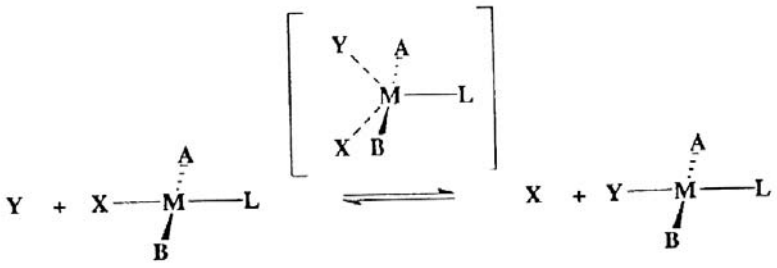
TRANS EFFECT IN PLATINUM(II) COMPLEXES AS MEASURED BY BUILT IN MOLECULAR GAUGES

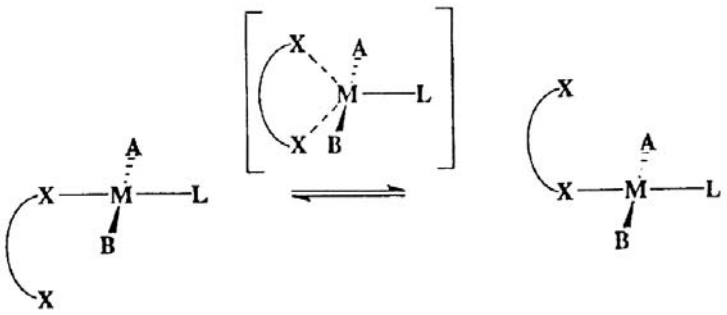
FRANCESCO PAOLO FANIZI - GIOVANNI NATILE

The task of compiling a reliable trans effect series, which could be useful for rationalizing and predicting inorganic reaction pathways, has involved more than one generation of inorganic chemists. In traditional substitution reactions (scheme 1), being the entering and leaving groups different, the effect of **L** on the reaction rate can be related either to the bond making or to the bond breaking depending upon which of the above processes is rate determining.



Scheme 1

As a consequence traditional trans effect series lack of general validity but depend upon the substitution reaction considered (i.e. the nature of **X** and **Y**). In order to overcome this problem, the entering and leaving ligand in the position trans to the ligand under test should be exactly the same. This condition has been recently used in a theorical work,[1] and can be accomplished by studying the intramolecular rate of exchange between the two ends of a monocoordinate symmetric bidentate ligand trans to the ligand whose trans effect is under test (scheme 2).[2]



Scheme 2

This dynamic process, can be investigated by variable temperature NMR spectroscopy. The exchange rate and $\Delta G^{\ddagger}$ can be easily obtained from line shape analysis of the spectra [for example for $\mathbf{M} = Pt$, $\mathbf{X} - \mathbf{X}$ =2,9-Me_2 − 1, 10-phenanthroline, $\mathbf{A} = \mathbf{B} = PPh_3$, $\Delta G^{\ddagger}$ (kcal/mol) are: 10.4 (**L**=CI), 9.3 (**L**=Br), 7.8 (**L**=I)]. Moreover for such an intramolecular process the enthropic contribution is expected to be small. The steric and electronic properties of the bidentate ligand can be tuned in order the head to tail rearrangement to be measurable for ligands of very different trans effect. The effects of the total charge of the complex and of the cis ligands can also be investigated.

REFERENCES

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Dipartimento Farmaco-Chimico
Università di Bari
via E. Orabona 4, 70125, Bari (Italy)