



UNIVERSITA' DI MESSINA
FACOLTA' DI SCIENZE

Dipartimento di Chimica Inorganica, Analitica
e Struttura Molecolare



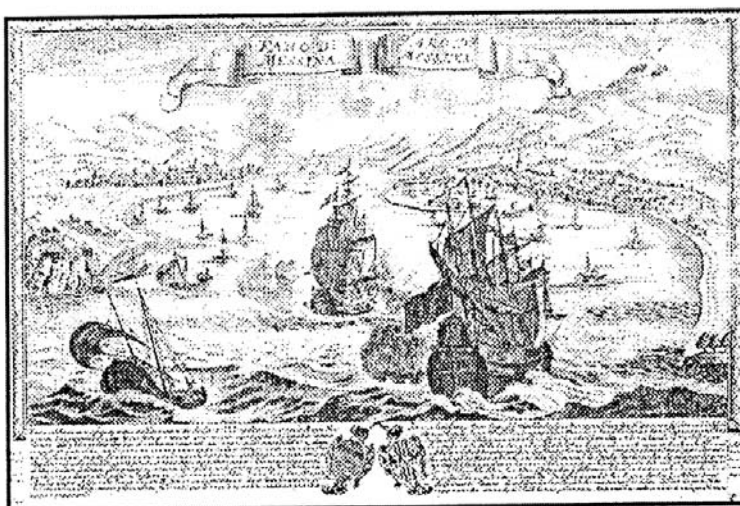
Società Chimica Italiana
visione di Chimica Inorganica



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

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



MESSINA 30-31 MAGGIO 1994
Aula dell'Accademia

**EQUILIBRIUM STUDIES OF α -DIIMINE DISPLACEMENT
IN CATIONIC ALLYLPALLADIUM(II)
COMPLEXES BY MONODENTATE N-DONOR LIGANDS
AND THE MECHANISM OF ALLYL
AMINATION BY TRIETHYLAMINE AND PYRIDINE**

L. CANOVESE - F. VISENTIN - P. UGUAGLIATI
F. DI BIANCA - S. ANTONAROLI - B. CROCIANI

In the cationic complexes $[\text{Pd}(\eta^3\text{-all})(\text{N-N}')]\text{ClO}_4$ ($\text{N-N}'=1,2$ -bis(imino)ethanes or pyridine-2-carbaldimines) the chelated α -diimine is rapidly and reversibly displaced by secondary amines (N-methylaniline, morpholine, piperidine), triethylamine, and 4-substituted pyridines. The observed equilibrium constants K_e increase with increasing basicity and decreasing steric requirements of the entering N-donor ligand. They strongly depend on the α -diimine and decrease in the order $\text{RN}=\text{CH}-\text{CH}=\text{NR} \gg \text{RN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NR} = \text{py-2-CH}=\text{NR}$ ($\text{R}=\text{C}_6\text{H}_4\text{OMe-4}$). The complex $[\text{Pd}(\eta^3\text{-all})(\text{py-2-CH}=\text{NC}_6\text{H}_4\text{OMe-4})]\text{ClO}_4$ undergoes a slow allyl amination by triethylamine or pyridine (A) in the presence of fumaronitrile (fn), yielding $[\text{Pd}(\eta^2\text{-fn})(\text{py-2-CH}=\text{NC}_6\text{H}_4\text{OMe-4})]$ and $\text{Et}_3\text{N}^+-\text{CH}_2\text{CH}=\text{CH}_2$ or $\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2\text{CH}=\text{CH}_2$. Kinetic studies show that the pseudo-first order rate constants of amination (k_{obs}) are given by $k_{obs}=k_2[\text{A}]$,

suggesting a direct bimolecular attack of A on the η^3 -allyl ligand. The amination hardly proceeds in the presence of the less activated olefin dimethyl fumarate (dmf). The π -accepting properties of the olefinic ligands play an important role also in the oxidative addition of $\text{Et}_3\text{N}^+-\text{CH}_2\text{CH}=\text{CH}_2$ or $\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2\text{CH}=\text{CH}_2$ to $[\text{Pd}(\eta^2\text{-ol})(\text{py-2-CH}=\text{NC}_6\text{H}_4\text{OMe-4})]$ (ol=fn, dmf), i.e. the reverse of the amination reaction.

Luciano Canovese - Fabiano Visentin - Paolo Uguagliati
Dipartimento di Chimica
Università di Venezia, Italy

Francesca Di Bianca - Bruno Crociani
Dipartimento di Chimica Inorganica
Università di Palermo, Italy

Simonetta Antonaroli
Dipartimento di Scienze
e Tecnologie Chimiche II
Università di Roma, Italy