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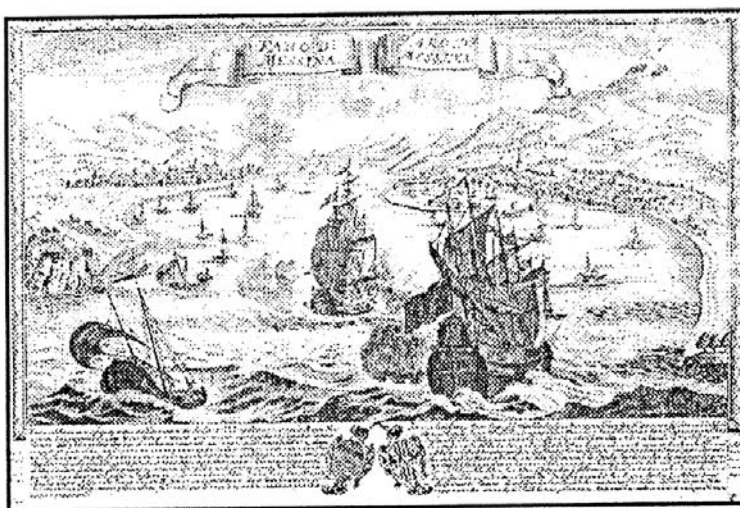
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Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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**THE APPLICATION OF NMR SPECTROSCOPY
TO THE STUDY OF PLATINUM
AND PLATINUM GROUP COMPOUNDS**

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The paper will consist of two parts. Firstly, the use of NMR spectroscopy to study platinum complexes will be reviewed, and then recent results from my own research will be discussed.

The use of 1H , ^{13}C , ^{15}N , ^{31}P , and ^{195}Pt NMR spectroscopy to examine platinum complexes will be examined. The role of techniques such as NOE, COSY, INEPT, DEPT $^{13}C\{^1H\}$ correlation, and inverse detection will be discussed.

Extensive use has been made of NMR spectroscopy to detect reaction intermediates. Recently this has been particularly successful for the hydrogenation catalyst, $[RuCl(H)(PPh_3)_3]$. We have already shown that $[RuCl(H)(PPh_3)_3]$ reacts with cyclohepta-1,3-diene to give $[(\eta^3 - C_7H_{11})RuCl(PPh_3)_2]$ and then $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ ^{1,2}. Further investigation of $[(\eta^5 C_7H_9)RuCl(PPh_3)_2]$ shows that it undergoes dissociative PPh_3 exchange, even at $-30^\circ C$, to give the highly reactive $[(\eta^5 - C_7H_9)RuCl(PPh_3)]$. Treatment of $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ with H_2 yields first $[(\eta^3 - C_7H_{11})RuCl(PPh_3)_2]$ and then $[Ru_2H_4Cl_2(PPh_3)_4]$,

which always contains some $[RuCl(H)(PPh_3)_3]$. This solution is a more powerful hydrogenation catalyst than $[RuCl(H)(PPh_3)_3]$. Alternatively, $[RuCl(H)(PPh_3)_3]$ can be produced by adding one equivalent of PPh_3 to $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ before hydrogenation. As solid $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ is indefinitely stable in air, it provides a convenient precursor for the $[RuCl(H)(PPh_3)_3]$ hydrogenation catalyst.³

The mechanism of carbonyl scrambling in $[Ir_4(CO)_{11}L]$, $L = PEt_3$, PH_2Ph , and $PHPh_2$ has been investigated using magnetization transfer measurements. It is shown that there are two main mechanisms operating, and there is a substantial barrier separating the bridged and unbridged intermediates.^{4,5}

The trigonal twist mechanism has been demonstrated in $[RuH_2(CO)(PPh_3)]$ using EXSY.⁶ It will be shown how exchange between lines of multiplets yields specific information on chemical exchange mechanisms.

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