

Ruthenium Complexes of Nitrogen- and Sulfur-Containing Heterocycles

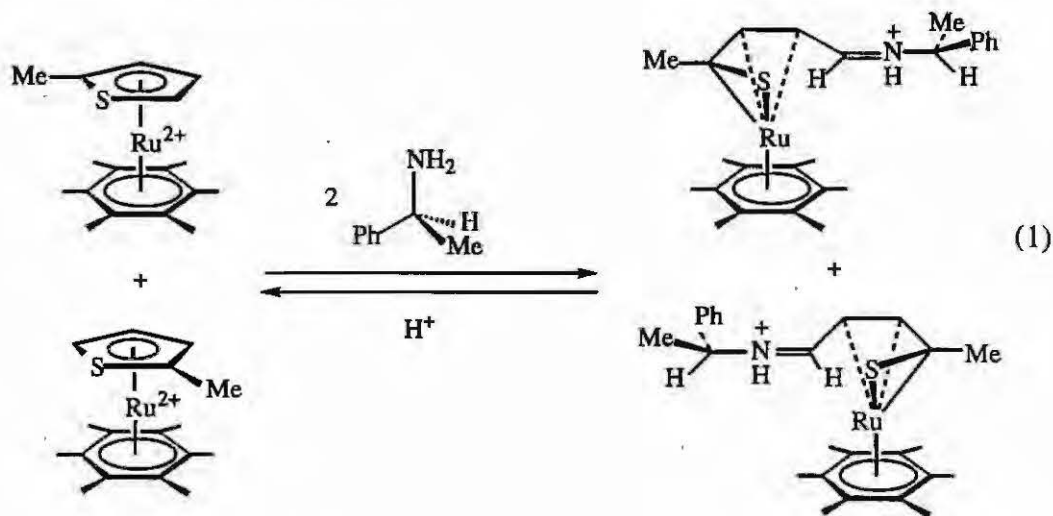
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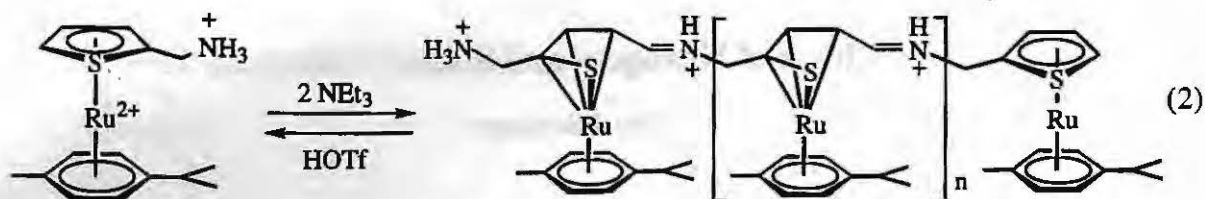
In the United States the conventional crude petroleum reserves, that is those which are relatively inexpensive to acquire and process, were depleted by 21.3% between 1978 and 1991.¹ This decrease in domestic oil reserves is reflected by the fact that the crude oil pool has gotten heavier. Heavier crudes are associated with higher boiling point hydrocarbon fractions as well as high levels of sulfur, nitrogen, and metal constituents. Although light crude oils are still being imported, industrial interest in "bottom-of-the-barrel" crudes² is manifested by the increasing capability of the U.S. refiners to process these stocks. Of paramount importance in the upgrading of petroleum is the removal of organosulfur, organonitrogen, and organometallic constituents. Heteroatoms and metals present in the crudes tend to poison/passivate cracking and reforming catalysts.³ Combustion of heteroatoms also presents environmental problems due to the formation of SO_x and NO_x which contribute to acid rain production. Our interest in these processes/problems has focused on the interactions of heterocycles with Ru metal centers and the subsequent reactivities of these complexes.

The sandwich complexes [(C₆Me₆)Ru(2-RC₄H₃S)](OTf)₂, prepared by reaction of (C₆Me₆)Ru(OTf)₂ and 2-RC₄H₃S,⁴ are highly electrophilic. The thiophene ligands in these species react with (S)-(-)-α-methylbenzylamine to give a 1:1 mixture of diastereomeric iminium thiolato derivatives (eq 1). Isolation of the less polar diastereomer by chromatography followed by protonolysis regenerates optically pure π-complexes. This constitutes



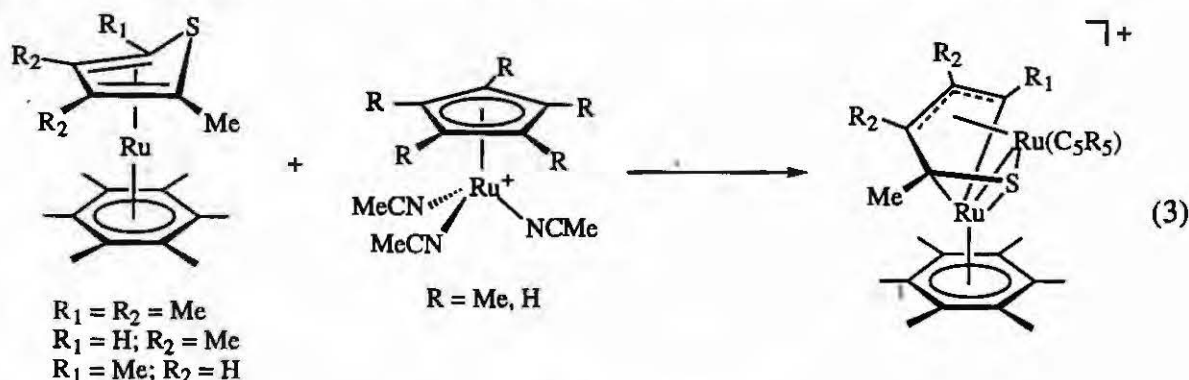
a fairly general method for the optical resolution of π-coordinated thiophene complexes.⁵ This separation was achieved for 2-MeC₄H₃S, 2-HOCH₂C₄H₃S, and 2,2'-(C₄H₃S)₂C₄H₃S derivatives. Base hydrolysis of (-)-[(C₆Me₆)Ru(2-RC₄H₃S)](OTf)₂ was found to be enantioselective and the resulting formyl thiolato derivatives isomerize with inversion of configuration at Ru, as confirmed by circular dichroism measurements.

π-Complexes of 2-substituted functionalized thiophenes, 2-RC₄H₃S, have been prepared where R = HOCH₂, HOCH₂CH₂, tBocNHCH₂, and NH₃⁺CH₂. The amine derivative must first be protected to prevent formation of simple σ-complexes such as (arene)Ru(NH₂CH₂C₄H₃S)₃²⁺. The π-complexed aminomethylthiophenes are interesting



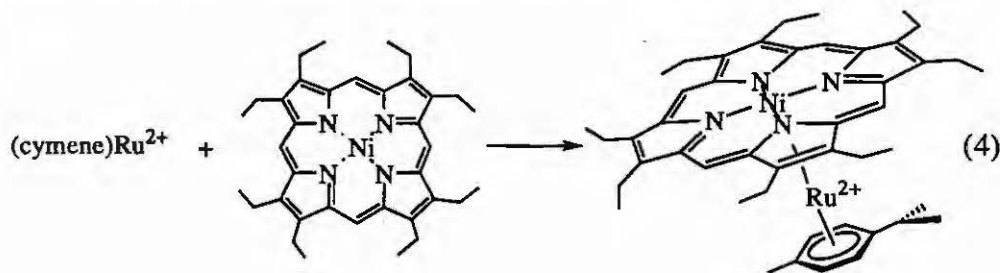
because they undergo intermolecular nucleophilic addition (eq 2) upon treatment with base to afford oligomeric species which have been identified spectroscopically.

Previous work had shown that protonation of the reduced thiophene complexes results in C-S bond scission, a key catalytic step in hydrodesulfurization.⁶ For example, the protonated thiophene complex $(C_6Me_6)Ru(\eta^4-C_4H_5S)^+$ exists in equilibrium with a thiapentadienyl derivative.⁷ Unfortunately, this equilibrium is not observed for the corresponding alkyl-substituted thiophene derivatives, which are of greater industrial relevance. However, solutions of $(C_6Me_6)Ru(\eta^4-C_4Me_4S)$ when treated with $[(C_5H_5)Ru(MeCN)_3]PF_6$ afford a species in which a carbon-sulfur bond is broken and the thiophene is simultaneously coordinated in an η^3 - and η^4 -manner to the $(C_6Me_6)Ru$ and $(C_5H_5)Ru$ units, respectively (eq 3). Single crystal X-ray data shows that the complex,



$[(C_5H_5)Ru(\eta^4:\eta^3-C_4Me_4S)Ru(C_6Me_6)]PF_6$ is asymmetric, in accord with the 1H and ^{13}C NMR spectra.⁸ In these reactions we view $(C_5H_5)Ru^+$ as a source of a "super proton" which is capable of cleaving the C-S bonds of highly substituted thiophenes.

In petroleum refining, the organometallic species of greatest consequence are the petroporphyrins.⁹ We wished to investigate the interaction of these metalloporphyrins with metal centers so as to model their interactions with metal-containing HDS catalysts. Treatment of $(cymene)Ru^{2+}$ with $Ni(OEP)$ gives a complex in which the $Ru(II)$ center is π -bound to a pyrrolide unit on the periphery of the metalloporphyrin, $[(cymene)Ru\{Ni(OEP)\}]^{2+}$ (eq 4).¹⁰ This bonding mode was confirmed spectroscopically as well as by a single crystal X-ray



diffraction study. In contrast to the behavior of the Ru-Ni complex, protonolysis of [(cymene)Ru{Zn(OEP)OTf}]OTf results in the removal of Zn(II) to give a demetallated complex [(cymene)Ru{H_x(OEP)}]ⁿ⁺ which was detected spectroscopically.

References

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