Journal of Organometallic Chemistry, 107 (1976) C46—C48

Preliminary communication

REACTION OF [η^6-$C_6H_6RuCl_2$]$_2$ AND [η^5-$C_5Me_5RhCl_2$]$_2$ WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

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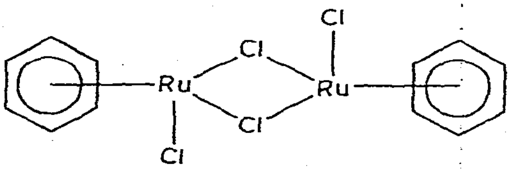
(Received December 27th, 1975)

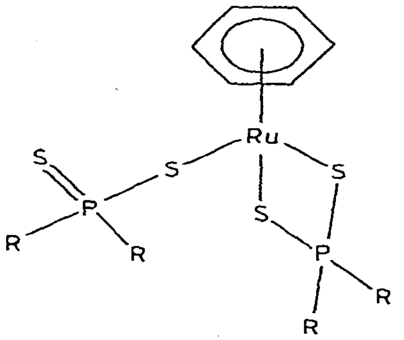
Summary

The dithioacid ligand complexes [η^6-$C_6H_6Ru(S_2PR_2)_2$], [η^5-$C_5Me_5Rh(S{-}S)_2$], [$(S{-}S)^- = {}^-S_2PR_2, {}^-S_2CNR_2, {}^-S_2COR$], [$\eta^5$-$C_5Me_5RhCl(S_2CNR_2)$] and [$\eta^5$-$C_5Me_5Rh(S_2PMe_2)(S_2CNMe_2)$] have been synthesised by reaction of [η^6-$C_6H_6RuCl_2$]$_2$ and [η^5-$C_5Me_5RhCl_2$]$_2$ respectively with Na(S—S).

In recent papers, the synthesis of the complexes *cis*-[$Ru(S{-}S)_2$ diene] [$(S{-}S)^- = {}^-S_2CNR_2$ [1,2], ${}^-S_2PR_2$ [2]; diene = 1,5-C_8H_{12}, C_7H_8] by reaction of [$RuCl_2$(diene)]$_n$ with Na(S—S) have been described. In this note, we wish to report the results of the related reactions between [η^6-$C_6H_6RuCl_2$]$_2$ (I) and various sulphur containing nucleophiles. Although the reactions of I with various monodentate nucleophiles have been described [3,4], the only other published work involving reaction with potential bidentate nucleophiles is that of $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 4$) giving [η^6-$C_6H_6RuCl_2(Ph_2PCH_2PPh_2)$] and [$(\eta^6$-$C_6H_6RuCl_2)_2\{Ph_2P(CH_2)_4PPh_2\}$] with mono- and bi-dentate coordination respectively [3].



(I)



(II)

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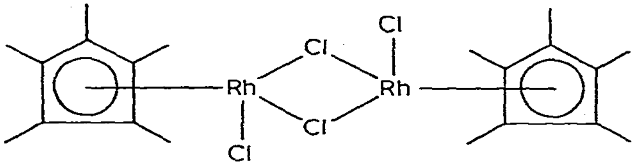
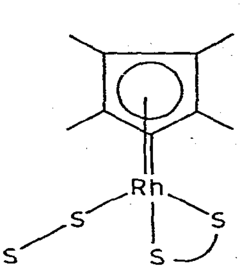
Reaction of I with NaS_2PR_2 in water (1:2 molar ratio) gives monomeric complexes of formula $[\eta^6\text{-}C_6H_6Ru(S_2PR_2)_2]$ (R = Me, Ph, OMe, OEt). ^1H and ^{31}P NMR studies reveal that these compounds are best formulated with mono- and bi-dentate ligands [structure (II)], e.g. for $^-S_2PMe_2$, the ^1H NMR spectrum at 303 K consists of three doublets of relative intensity (2; 1; 1) ($^2J(PH)$ 12.0 Hz) in addition to a singlet at δ 5.88 ppm ($\eta^6\text{-}C_6H_6$). However, although they are stereochemically rigid at room temperature, ready decomposition in solution as indicated by the appearance of free benzene (^1H and ^{13}C NMR) and $^-S_2PR_2$ (^{31}P NMR) prohibits a detailed examination of possible rearrangement processes in these complexes. Furthermore, reaction of I with dialkyldithiocarbamate and *O*-alkyldithiocarbonate anions gives paramagnetic products containing no coordinated benzene.



(III)



(IV)

Therefore, since I does not give a very wide range of arene complexes containing dithioacid ligands, we have investigated similar reactions with the isoelectronic $[\eta^5\text{-}C_5Me_5RhCl_2]_2$ (III) [5]. Thus, III reacts with $^-S_2PR_2$ (1:1 mole ratio) (R = Me, Ph) to give $[\eta^5\text{-}C_5Me_5Rh(S_2PR_2)_2]$ (IV). Unlike I, however, III reacts with the stronger nucleophiles $^-S_2CNR_2$ and ^-S_2COR, without loss of the π-bonded ring, to give the analogous $[\eta^5\text{-}C_5Me_5Rh\text{-}(S\text{—}S)_2]$ (IV). NMR studies at ambient temperature confirm the presence of inequivalent dithioacid ligands in all these compounds and variable temperature studies at higher temperatures reveal that interconversion of mono- and bi-dentate dithioacid ligands occurs. A detailed kinetic line-shape analysis of this process is now in progress. Reaction of III with NaS_2CNMe_2 (1:1 mole ratio) gives $[\eta^5\text{-}C_5Me_5RhCl(S_2CNMe_2)]$, from which the mixed dithioacid complex $[\eta^5\text{-}C_5Me_5Rh(S_2PMe_2)(S_2CNMe_2)]$* can be synthesised. NMR studies show the latter to have bidentate $^-S_2CNMe_2$ and unidentate $^-S_2PMe_2$ groups.

Acknowledgement

We thank Johnson—Matthey Ltd for loans of ruthenium trichloride and rhodium trichloride and the S.R.C. (D.R.R.) for a research studentship.

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*All the compounds reported in this note have been characterised satisfactorily by elemental analyses and molecular weight determinations.

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