A Novel Reaction of Coordinated Vinylidenes: Coupling with Hydrogen Sulfide to give a η^1-Thioaldehyde

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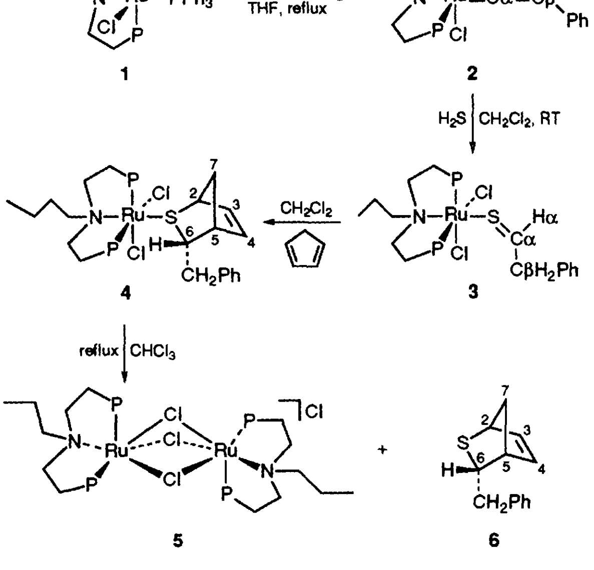
The Ru^{II} fragment $[(PNP)RuCl_2]$ assists the coupling of phenylacetylene with H_2S to give 2-phenylethanethial $[PNP = CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2]$ in a reaction that is initiated by alk-1-yne to vinylidene tautomerism at ruthenium, followed by electrophilic attack of H_2S on the vinylidene ligand; 2-phenylethanethial is recovered as either η^1-S-ligand or *endo*-6-benzyl-1-thiabicyclo[2.2.1]hept-3-ene ligand, and the latter molecule is formed *via* a stereoselective Diels–Alder reaction between cyclopentadiene and the η^1-2-phenylethanethial complex.

The chemistry of transition metal vinylidenes has been intensely investigated over the past two decades.[1] Interest in these compounds stems from both their wide potential in organic and organometallic syntheses[2] and their implication in several homo- and hetero-geneous catalytic processes.[3] The reactivity of metal vinylidene complexes towards small inorganic molecules, *e.g.* O_2,[4] H_2O[5] and heteroallenes,[6] remains an undeveloped although attractive area of organometallic chemistry. However, with reference to the large availability of these strategic inorganic molecules as well as the ubiquity of vinylidene derivatives along the series of transition metals, investigation of these reactions remains an exciting and prosperous area of vinylidene chemistry.

Here we report on the reaction between a Ru^{II} vinylidene complex and H_2S, which provides unprecedented access to η^1-2-phenylethanethial.

Heating *mer,trans*-$[(PNP)RuCl_2(PPh_3)]$[7] **1** in THF with an excess of phenylacetylene at reflux results in quantitative precipitation of the vinylidene *fac,cis*-$[(PNP)RuCl_2\{C{=}C(H)Ph\}]$† **2** as pale orange needles crystals, while triphenylphosphine remains in solution. Bubbling H_2S into a refluxing CH_2Cl_2 solution of **2** for 2 h quantitatively converts the vinylidene complex to *fac,cis*-$[(PNP)RuCl_2\{\eta^1\text{-}S{=}CH(CH_2Ph)\}]$ **3**.† The presence of a η^1-2-phenylethanethial ligand in **3** is unambiguously shown by both $^{13}C\{^1H\}$ and ^1H NMR spectroscopy[8] [δC_α 230.34; δC_β 54.14; δH_α 12.10, to $^3J(HH)$ 7.9 Hz] and the reaction with cyclopentadiene. Compound **3** in CH_2Cl_2 reacts at room temperature with an excess of 1,3-cyclopentadiene to give *fac,cis*-$[(PNP)RuCl_2\{\eta^1\text{-}$*endo*-$SC_6H_7(CH_2Ph)\}]$ **4** as dark red microcrystals.† The Diels–Alder reaction with the diene is stereoselective and occurs with a preference for the *endo* isomer, as shown by the chemical shift and coupling constants of H_6 in the η^1-*S*-6-benzyl-1-thiabicyclo[2.2.1]hept-3-ene ligand [δH_6 4.91, td, $^3J(H_6H_5)$ 4.0, $^3J(H_6H_{Bz})$ 8.0 Hz].[8,9] The phenylethanethial/cyclopentadiene adduct can be removed from the metal by simply heating a $CHCl_3$ solution of **4** to reflux. As a result, the unsaturated metal fragment $[(PNP)RuCl_2]$ dimerizes to the known face-sharing bioctahedral complex $[Ru_2(\mu\text{-}Cl)_3(PNP)_2]Cl$ **5**,[7] while *endo*-6-benzyl-1-thiabicyclo-[2.2.1]hept-3-ene† can be isolated by TLC (Al_2O_3, eluent Et_2O). The dimer **5** can also be obtained by refluxing **3** in $CHCl_3$. However, in the absence of a specific reagent for trapping the phenylethanethial, this spontaneously oligomerises.[10]



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Footnote

† Satisfactory spectroscopic data was obtained for all compounds.

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