Molecular Mercaptan (Thiol) Complexes: The Synthesis of the *tert*-Butanethiol Complexes [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)(Bu^tSH)]PF_6 and [Ru(η^5-C_5H_5)(dppm)(Bu^tSH)]PF_6 and the X-Ray Single Crystal Structure of [Ru(η^5-C_5H_5)(dppm)(Bu^tSH)]PF_6 [dppm = bis(diphenylphosphino)methane]

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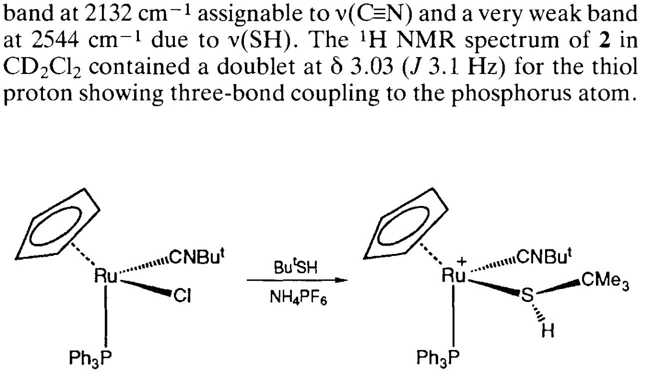
The reaction of the chlorides [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)(Cl)] and [Ru(η^5-C_5H_5)(dppm)(Cl)] with Bu^tSH in methanol containing NH_4PF_6 leads to the isolation of the complexes [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)(Bu^tSH)]PF_6 **2** and [Ru(η^5-C_5H_5)(dppm)(Bu^tSH)]PF_6 **4** which both contain the intact thiol as a ligand.

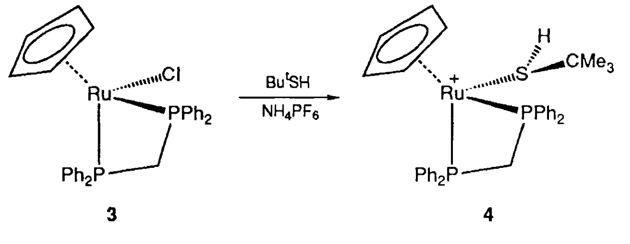
The recent preparation of stable molecular dihydrogen[1,2] and iodoalkane[3,4] complexes of those transition metals commonly found in homogeneous catalytic systems has led to a new understanding of the mechanisms of concerted oxidative addition. It was of interest to us to investigate the possibility of preparing complexes which contained other types of classical oxidative addends[5] as molecular ligands. Few examples of hydrogen sulphide acting either as a molecular ligand[6,7] or as an oxidative addend[8] exist and there are only four reports of a thiol acting as a ligand.[7,9,10,11] The unstable complex, [Ru(NH_3)$_5$(EtSH)](BF_4)$_2$, is relatively poorly characterised from a spectroscopic viewpoint,[7] while Treichel[9] has reported that [Fe(η^5-C_5H_5)(CO)$_2$(PhSH)]BF_4 is a strong acid. Rauchfuss[10] prepared [Ru(η^5-C_5H_5)(PPh_3)$_2$(Pr^nSH)]BF_4 using thiophene as the source of the n-propanethiol ligand and presented the crystal structure of this salt. Darensbourg[11] has recently reported the crystallographic characterisation of a molecular thiol complex, [Cr(CO)$_5$($HSBu^t$)]. Bergman[12] has prepared and crystallographically characterised the complex [Ir(η^5-C_5Me_5)(PMe_3)(SBu^t)(H)] where the molecular thiol form is not favoured. The preference for metal thiolato(hydrido) complex formation over that of the metal thiol complex has also been observed in complexes of molybdenum designed to model the metal centre of nitrogenase.[13]

We have previously demonstrated the ability of the [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)]$^+$ and [Ru(η^5-C_5H_5)(dppm)]$^+$ (dppm = bis(diphenylphosphinomethane) moieties to stabilise dihydrogen and iodoalkanes as metal bound ligands[1,3] and now report the rational preparation of stable Bu^tSH complexes of these fragments.

Treatment of [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)Cl] **1** with Bu^tSH in the presence of methanolic NH_4PF_6 gave yellow crystals of [Ru(η^5-C_5H_5)(PPh_3)(Bu^tNC)(Bu^tSH)]PF_6 **2** in 48% yield. The IR spectrum of **2** contained *inter alia* a strong band at 2132 cm^{-1} assignable to ν(C≡N) and a very weak band at 2544 cm^{-1} due to ν(SH). The ^1H NMR spectrum of **2** in CD_2Cl_2 contained a doublet at δ 3.03 (*J* 3.1 Hz) for the thiol proton showing three-bond coupling to the phosphorus atom.



1 **2**



3 **4**

Bergman[12] has observed a similar coupling of 4.5 Hz in $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(SH)_2]$. Compound **2** could also be prepared by the reaction of the dihydrogen cation complex $\{[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Bu^tNC)(\eta^2\text{-}H_2)]PF_6\}$ with the thiol in dichloromethane.

The bis(diphenylphosphino)methane analogue $[Ru(\eta^5\text{-}C_5H_5)(dppm)(Bu^tSH)]PF_6$ **4** was prepared analogously from either the chloro-complex $[Ru(\eta^5\text{-}C_5H_5)(dppm)(Cl)]$ **3** or the dihydrogen cation $[Ru(\eta^5\text{-}C_5H_5)(dppm)(\eta^2\text{-}H_2]PF_6$ in 62 and 34% yield, respectively. The sulphur–hydrogen stretching mode of **4** was too weak to observe by IR spectroscopy but the thiol hydrogen was observed at δ 2.74 as a triplet (*J* 10.7 Hz) in its ^1H NMR spectrum in CD_2Cl_2. The mass spectrum (FAB) of **4** showed the parent cation at *m/z* 641.

Carefully prepared solutions of both **2** and **4** showed no evidence of free thiol or the presence of a hydrido(thiolate) isomer by ^1H NMR spectroscopy over the range 185 to 308 K. The triplet resonance for the thiol proton of **4** was unchanged down to 185 K; the failure to observe the expected doublet of doublets is probably due to degeneracy of the phosphorus–hydrogen coupling constants rather than a low rotational barrier for the thiol ligand about the metal–sulphur bond. This barrier in the dimethyl sulphide complex,[14] $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Bu^tNC)(SMe_2)]PF_6$ for example, has the value $\Delta G^{\ddagger}_{257} = 52.4$ KJ mol^{-1}.

In contrast to many other cationic complexes of the $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)(Bu^tNC)]^+$ and $[Ru(\eta^5\text{-}C_5H_5)(dppm)]^+$ moieties, the solutions were air-sensitive and rapidly changed from yellow to bright purple on exposure to air indicating an increased sensitivity to aerial oxidation of the thiol on coordination.

The X-ray single crystal structure† of **4** was determined at 233 K to confirm the integrity of the thiol ligand and is shown in Fig. 1 together with selected bond lengths and bond angles. The geometry at ruthenium is pseudo-octahedral as expected with the *tert*-butyl group pointing away from the phenyl rings C(31)–C(36) and C(11)–C(16). The sulphur-bound hydrogen was located and freely refined; the angles at the sulphur atom confirm pyramidal geometry similar to that found for $[Cr(CO)_5(HSBu^t)]$.[11] The ruthenium–sulphur bond-length of 2.371(2) Å is equal to the sum of the covalent radii of the elements confirming that the bonding is of a σ-donor type with little or no backbonding; this bond length in $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(Pr^nSH)]BF_4$ was 2.377(2) Å.[10] The sulphur–hydrogen bond at 1.349(77) Å compares with the values of 1.25(6) and 1.2(1) Å reported by Rauchfuss[10] and Darensbourg,[11] respectively. The value of *r*(S–H) determined by rotational spectroscopy in sulphane (H_2S_2) is 1.327(3) Å.[15]

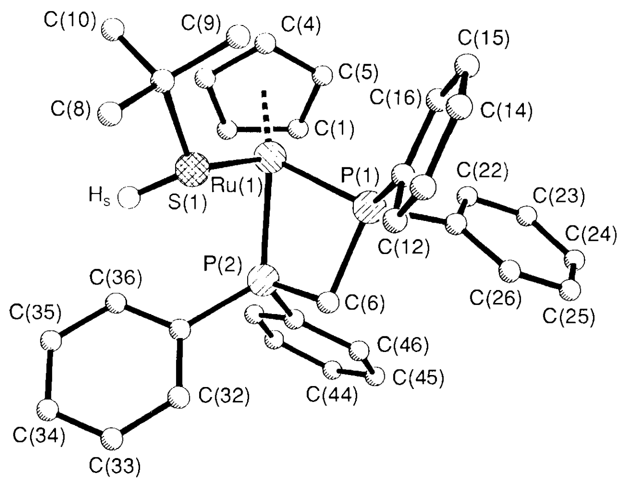


Fig. 1 Molecular structure of the cation in **4**. Selected bond lengths (Å) and angles (°): Ru(1)–S(1) 2.371(2), Ru(1)–P(1) 2.314(2), Ru(1)–P(2) 2.289(2), S(1)–C(7) 1.870(8), S(1)–H_s 1.349(77); S(1)–Ru(1)–P(1) 88.2(1), S(1)–Ru(1)–P(2) 83.7(1), P(1)–Ru(1)–P(2) 70.4(1), Ru(1)–S(1)–C(7) 121.1(3), Ru(1)–S(1)–H_s 108.1(34), H_s–S(1)–C(7) 100.3(33).

The isolation of these stable molecular thiol complexes emphasises the reluctance of these d^6 Ru^{II} complexes to undergo oxidative addition even in the presence of the very acidic S–H bond. The general applicability of the synthetic routes used here to the isolation of complexes of related and more reactive oxidative addends is being pursued currently.

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† *Crystal data* for $C_{34}H_{37}F_6P_3SRu$: *M* = 785.7, monoclinic, *Cc* (No. 9), *a* = 10.143(3), *b* = 18.262(5), *c* = 19.067(5) Å, β = 92.81(2)°, *U* = 3527(15) Å^3, D_c = 1.479 g cm^{-3}, *Z* = 4, *F*(000) = 1600, μ(Mo-Kα) = 6.80 cm^{-1}. A yellow cut block of dimensions 0.26 × 0.21 × 0.14 mm was used for measurement at 233 K. Intensity data in the range $3° < 2\theta < 65°$ were collected using a θ–2θ scan technique on a Nicolet R3m/V diffractometer. The intensities of three reflections measured periodically showed a decrease of less than 2% over the data collection. An empirical absorption correction was applied on the basis of 462 azimuthal scan data. A total of 6907 reflections were collected of which 6722 were independent, and 4663 for which $I > 2.5\,\sigma(I)$ were used in the refinement. The ruthenium, phosphorus and sulphur atoms were located from a Patterson map. Subsequent electron-density difference syntheses located all remaining non-hydrogen atoms. The hydrogen atoms other than H_s were placed in calculated positions and were refined isotropically using a riding model. All non-hydrogen atoms of the cation and the PF_6 anion were refined anisotropically. The thiol hydrogen H_s was located by an electron-density difference synthesis and was freely refined isotropically. At convergence $R = 4.62$ and $R_w = 5.04\%$ $w = [\sigma^2(F) + 0.0006F^2]^{-1}$, $S = 1.25$, $\Delta/\sigma < 0.001$. The successful refinement confirmed the choice of the space-group *Cc* over that of *C*2/*c*. Calculations were performed using the SHELXTL-PLUS program package on a MICROVAX II. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.