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S–H Bond cleavage *versus* thiol co-ordination in half-sandwich ruthenium complexes †

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The complex [RuCp*Cl(dippe)] [dippe = 1,2-bis(diisopropylphosphino)ethane] underwent oxidative addition of H_2S in MeOH affording the ruthenium(IV) hydridothiol $[RuCp^*H(SH)(dippe)]^+$, which was isolated as its $[BPh_4]^-$ salt **1**. No oxidative addition has been observed in the course of the reaction of [RuCpCl(dippe)] with H_2S and $NaBPh_4$ in MeOH, and the binuclear disulfido derivative $[\{RuCp(dippe)\}_2(\mu\text{-}S_2)][BPh_4]_2$ **2** was obtained. The related derivative $[\{RuCp^*(dippe)\}_2(\mu\text{-}S_2)][BPh_4]_2$ **3** was obtained by aerial oxidation of **1**. At variance with this, the reaction of [RuCp*Cl(dippe)] and [RuCpCl(dippe)] with HSPh and $NaBPh_4$ in MeOH yielded respectively the ruthenium(III) thiolate complex $[RuCp^*(SPh)(dippe)][BPh_4]$ **4** and the extremely air-sensitive thiol adduct $[RuCp(HSPh)(dippe)][BPh_4]$ **5**. The latter is readily oxidized by atmospheric oxygen to the corresponding ruthenium(III) thiolate complex $[RuCp(SPh)(dippe)][BPh_4]$ **6**. The hydridometallothiol **1** as well as the thiolates **4** and **6** react with base affording respectively the neutral mercapto complex $[RuCp^*(SH)(dippe)]$ **7** and the neutral thiolate derivatives $[RuCp^*(SPh)(dippe)]$ **8** and $[RuCp(SPh)(dippe)]$ **9**. The reactivity of [RuCp*Cl(dippe)] and [RuCpCl(dippe)] towards pyridine-2-thiol and pyrimidine-2-thiol has also been examined.

Introduction

The activation of RS–H bonds by transition metals may occur following either a heterolytic cleavage of the S–H bond, or by homolysis resulting in the formation of H_2 and metallo- or sulfur-based radicals.[1] It has been reported that protonation of the sulfur atom of the thiolate ligand in anionic $[Fe(MeS)(CO)_3(PR_3)]^-$ (R = Et or OEt) affords the unstable thiol complexes $[Fe(MeSH)(CO)_3(PR_3)]$, which upon warming rearrange to their more stable hydridothiolate tautomers $[FeH(SR)(CO)_3(PR_3)]$. In the case of the PEt_3 derivative it was possible to detect the intermediate species $[Fe(\eta^2\text{-H–SR})(CO)_3(PEt_3)]$, invoking the first example of an "arrested" S–H bond in its path towards oxidative addition.[2] Hence, organic thiols may eventually form stable adducts with transition metal complexes,[1,3–6] or give rise more frequently to mononuclear or polynuclear thiolate complexes.[7–10] In the particular case of the H_2S molecule examples of oxidative addition to electron-rich metal centres are fairly common, but H_2S adducts remain rare.[11,12] One of the synthetic routes successfully used for the preparation of a H_2S adduct of ruthenium has involved protonation of the lone pair at sulfur in the neutral thiolate derivative $[RuCp(SH)(PPh_3)_2]$.[12] In a recent work we described the first example of oxidative addition of H_2S to Ru^{II} to yield the ruthenium(II) hydridothiolate complex $[RuCp^*H(SH)(PEt_3)_2][BPh_4]$, which was structurally characterized.[13] The relevance of this reaction is striking, given the reluctance of d^6 ruthenium(II) complexes to undergo oxidative addition.[4] However we failed in identifying any species resulting from the interaction of organic thiols such as HSPh with either $[RuCp^*Cl(PEt_3)_2]$ or $[RuCpCl(PEt_3)_2]$. We now show that the systems [RuCp*Cl(dippe)] and [RuCpCl(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) exhibit a behaviour towards H_2S quite similar to that of their PEt_3 counterparts, and it has been possible to prepare the new hydridometallothiol derivative $[RuCp^*H(SH)(dippe)][BPh_4]$. In the course of the reaction with HSPh no hydridothiophenolate complex $[RuCp^*H(SPh)(dippe)][BPh_4]$ was obtained, despite the fact that the S–H bond energy in HSPh (75 kcal mol^{-1}) is lower than in H_2S (90 kcal mol^{-1}), and that the former has an acidic character much stronger than the latter.[2] Instead the ruthenium(III) thiolate $[RuCp^*(SPh)(dippe)][BPh_4]$ was formed, most likely through the intermediacy of the unstable thiol adduct $[RuCp^*(HSPh)(dippe)][BPh_4]$. In the case of the cyclopentadienyl derivative it was possible to isolate the corresponding thiol complex prior to oxidation. In this work we describe the synthesis, characterization and chemical properties of all these species, complementing the study initiated on the chemistry of half-sandwich ruthenium complexes with sulfur-donor ligands.

Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. The solvents THF, Et_2O and light petroleum (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane was prepared according to reported procedures.[14] The complexes [RuCp*Cl(dippe)][15] and [RuCpCl(dippe)][16] were obtained as reported. The IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer, UV-vis using a Milton Roy Spectronic 3000 Diode Array. Fast atom bombardment mass spectroscopy (FAB-MS) was performed at the University of Cordoba on a high resolution VG Auto Spec spectrometer operating in the FAB+ mode (scan range 900–1800 atomic mass units) using *m*-nitrobenzyl alcohol as matrix at 20 °C, NMR spectra on Varian Unity 400 MHz or Gemini 200 MHz spectrometers. Chemical shifts are given in ppm from $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$). The phosphine protons for all compounds appeared in the corresponding ^1H NMR spectra as a series of overlapping multiplets in the range δ 0.5–3, and were not assigned. Magnetic moments were

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4309/

measured in solution by the Evans method.[17] Microanalyses were performed by the Serveis Científico–Tècnics, Universitat de Barcelona.

CAUTION: H_2S is extremely toxic, and all the preparations involving its use should be carried out in a well ventilated fume hood!

Preparations

[RuCp*H(SH)(dippe)][BPh$_4$] 1. Through a mixture of [RuCp*Cl(dippe)] (0.5 g, *ca.* 1 mmol) and an excess of $NaBPh_4$ (0.4 g) in MeOH (20 ml), a stream of H_2S was bubbled. A greenish yellow, crystalline precipitate was formed. The mixture was stirred under H_2S for 5 min and then filtered. The microcrystalline precipitate was washed with ethanol and light petroleum and dried *in vacuo*. Yield: 0.46 g, 58% (Found: C, 67.5; H, 8.23; S, 3.6. Calc. for $C_{48}H_{69}BP_2RuS$: C, 67.7; H, 8.11; S, 3.7%). IR: ν(SH) 2553 cm^{-1}. NMR: ^{1}H [$(CD_3)_2CO$], δ −9.42 (t, J 35.8, RuH), −2.35 (t, J 7 Hz, SH) and 1.87 (s, C_5Me_5); ^{31}P-{^{1}H}, δ 70.9 (s).

[{RuCp(dippe)}$_2$(μ-S$_2$)][BPh$_4$]$_2$ 2. *Method A.* Through a mixture of [RuCpCl(dippe)] (0.3 g, *ca*. 0.6 mmol) and an excess of $NaBPh_4$ (0.35 g) in MeOH (20 ml) a stream of H_2S was bubbled, in a fashion similar to that for compound **1**. A green precipitate was formed. The mixture was stirred under H_2S for 5 min and then filtered. The solids were washed with ethanol and light petroleum and dried *in vacuo*.

Method B. To a solution of [RuCpCl(dippe)] (0.19 g, 0.41 mmol) in EtOH (15 ml), $NaBPh_4$ (0.3 g, excess) and solid S_8 (0.015 g) were added. The mixture was stirred at room temperature for 18 h. The resulting green precipitate was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Yields: method A, 0.2 g, 43%; B, 0.23 g, 72% (Found: C, 66.5; H, 7.44; S, 4.0. Calc. for $C_{43}H_{57}BP_2RuS$: C, 66.3; H, 7.32; S, 4.1%). FAB-MS: *m*/*z* 921 (M − 2 [BPh$_4$]$^-$). UV/Vis (THF solution, λ_{max}/nm (ε, M^{-1} cm^{-1})): 825 (11626). NMR: ^{1}H [$(CD_3)_2CO$], δ 5.71 (s, C_5H_5); ^{31}P-{^{1}H}, δ 92.6 (s).

[{RuCp*(dippe)}$_2$(μ-S$_2$)][BPh$_4$]$_2$ 3. *Method A.* An acetone solution (15 ml) of complex **1** (0.2 g, *ca*. 0.24 mmol) was stirred in the air for 18 h at room temperature. Addition of EtOH and concentration using reduced pressure afforded a green solid, which was filtered off, washed with light petroleum and dried *in vacuo*.

Method B. To a solution of [RuCp*Cl(dippe)] (0.3 g, 0.56 mmol) in EtOH (20 ml), $NaBPh_4$ (0.35 g, excess) and solid S_8 (0.02 g) were added. The mixture was stirred at room temperature for 18 h. The resulting green precipitate was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Yields: method A, 0.14 g, 69%; method B, 0.34 g, 72% (Found: C, 67.7; H, 7.77; S, 3.6. Calc. for $C_{48}H_{67}BP_2RuS$: C, 67.9; H, 7.89; S, 3.8%). FAB-MS: *m*/*z* 1062 (M-2[BPh$_4$]$^-$). UV/Vis (THF solution, λ_{max}/nm (ε M^{-1} cm^{-1})): 789 (11930) and 360 (7790). NMR: ^{1}H [$(CD_3)_2CO$], δ 1.80 (t, J_{HP} = 1.2 Hz, C_5Me_5); ^{31}P-{^{1}H}, δ 78.3 (s).

[RuCp*(SPh)(dippe)][BPh$_4$] 4. To a solution of [RuCp*Cl(dippe)] (0.26 g, *ca.* 0.5 mmol) in MeOH (15 ml), HSPh (0.1 ml) and $NaBPh_4$ (0.3 g, excess) were added. A purple colour developed. The mixture was stirred for 2 h at room temperature, and a purple solid gradually formed. If air is admitted to the reaction mixture the reaction time shortens considerably and the yield increases. The purple microcrystalline precipitate was filtered off, washed with EtOH and light petroleum and dried *in vacuo*. Yield: 0.23 g, 50% (essentially quantitative if the reaction is performed in the presence of air) (Found: C, 69.7; H, 7.62; S, 3.3. Calc. for $C_{54}H_{72}BP_2RuS$: C, 70.0; H, 7.78; S, 3.4%). IR: ν(C=C) 1575 cm^{-1}. μ_{eff} = 2.4 μ_B at 295 K.

[RuCp(HSPh)(dippe)][BPh$_4$] 5. To a solution of [RuCpCl(dippe)] (0.23 g, 0.5 mmol) in MeOH (15 ml), HSPh (0.1 ml) and $NaBPh_4$ (0.3 g, excess) were added. A golden brown precipitate was formed almost immediately. The mixture was stirred for 15 minutes at room temperature. The product was filtered off, washed with EtOH and light petroleum and dried *in vacuo*. Yield: 0.34 g, 79% (Found: C, 68.4; H, 7.51; S, 3.5. Calc. for $C_{49}H_{63}BP_2RuS$: C, 68.6; H, 7.40; S, 3.7%). IR: ν(SH) 2483, ν(C=C) 1577 cm^{-1}. NMR [$(CD_3)_2CO$]: ^{1}H, δ 2.90 (s, *H*SPh), 4.62 (s, C_5H_5), 7.13, 7.24, 7.30 (m, SC_6H_5). ^{31}P-{^{1}H}, δ 93.7 (s).

[RuCp(SPh)(dippe)][BPh$_4$] 6. This compound was obtained by carrying out under atmospheric oxygen the procedure described for **5**. It was also prepared by exposing to air an acetone solution of **5**, followed by addition of EtOH, concentration and cooling to −20 °C. Yield: *ca*. 75% (Found: C, 68.7; H, 7.36; S, 3.5. Calc. for $C_{49}H_{62}BP_2RuS$: C, 68.7; H, 7.29; S, 3.7%). IR: ν(C=C) 1575 cm^{-1}. μ_{eff} = 2.1 μ_B at 302 K.

[RuCp*(SH)(dippe)] 7. To a solution of complex **1** (0.42 g, *ca.* 0.36 mmol) in tetrahydrofuran (15 ml), lithium diisopropylamide (LDA, 0.25 ml of a 1.5 M solution in cyclohexane, *ca*. 0.38 mmol) was added. The mixture was stirred for 10 min at room temperature. The solvent was removed *in vacuo*, and the residue extracted with toluene. The solution was filtered through Celite, concentrated and then light petroleum was added. The yellow-orange crystalline product was collected by filtration, washed with a small amount of light petroleum and dried *in vacuo*. Yield: 0.09 g, 48% (Found: C, 53.9; H, 8.83; S, 5.9. Calc. for $C_{24}H_{48}P_2RuS$: C, 54.2; H, 9.04; S, 6.0%). IR: ν(SH) 2540 cm^{-1}. NMR: ^{1}H (C_6D_6), δ −3.95 (t, J 6 Hz, SH) and 1.75 (s, C_5Me_5); ^{31}P-{^{1}H}, δ 82.7 (s).

[RuCp*(SPh)(dippe)] 8. A solution of complex **4** (0.35 g, 0.38 mmol) in tetrahydrofuran (10 ml) was treated with an excess of solid KOBu^t. A change from purple to orange was immediately observed. The mixture was stirred at room temperature for 10 min. Then the solvent was removed *in vacuo*. The residue was extracted with toluene, and the solution filtered through Celite. Concentration, addition of light petroleum and cooling to −20 °C afforded orange crystals, which were filtered off and dried. Yield: 0.15 g, 66% (Found: C, 58.9; H, 8.78; S, 5.1. Calc. for $C_{30}H_{52}P_2RuS$: C, 59.3; H, 8.62; S, 5.3%). IR: ν(C=C) 1573 cm^{-1}. NMR: ^{1}H (C_6D_6): δ 1.74 (s, C_5Me_5); 6.95 (t), 7.07 (t), 7.71 (m) (SC_6H_5). ^{31}P-{^{1}H}, δ 77.6 (s).

[RuCp(SPh)(dippe)] 9. A procedure analogous to that used for complex **8** was followed, starting either from the thiol adduct **5**, or from the ruthenium(III) thiolate **6**. Yield: *ca.* 60%. (Found: C, 60.1; H, 7.98; S, 5.9. Calc. for $C_{25}H_{42}P_2RuS$: C, 55.9; H, 7.87; S, 5.9%). IR: ν(C=C) 1569 cm^{-1}. NMR [$(CD_3)_2CO$, 213 K]: ^{1}H, δ 4.73 (s, C_5H_5), 6.65, 6.87 and 7.24 (m br, SC_6H_5). ^{31}P-{^{1}H}, δ (213 K) 91.2 (s), (298 K) 91.5 (s br, $\delta\nu_{1/2}$ = 805 Hz).

[RuCp*(SC$_5$H$_4$N)(dippe)][BPh$_4$] 10. To a solution of [RuCp*Cl(dippe)] (0.16 g, *ca.* 0.3 mmol) in EtOH (15 ml), pyridine-2-thiol (HSPy, 0.04 g) and $NaBPh_4$ (0.3 g) were added. A red colour immediately developed. The mixture was stirred for 15 min at room temperature then, concentrated and cooled to −20 °C. A red-brown crystalline precipitate was obtained. It was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Yield: 0.19 g, 70% (Found: C, 68.4; H, 7.85; N, 1.4; S, 3.4. Calc. for $C_{53}H_{72}BNP_2RuS$: C, 68.5; H, 7.76; N, 1.5; S, 3.4%). IR: ν(C=C) 1561 cm^{-1}. NMR [$(CD_3)_2CO$]: ^{1}H, δ 1.77 (t, J_{HP} = 1.2 Hz, C_5Me_5), 12.10 (s, br, NH), 8.19 (br, 2 H), 7.64 (m) and 7.08 (m); ^{31}P-{^{1}H}, δ 74.1 (s).

[RuCp(SC$_5$H$_4$N)(dippe)][BPh$_4$] 11. A procedure analogous to that for complex **10** was followed, starting from [RuCpCl(dippe)] (0.13 g, 0.28 mmol). The product was obtained as an

orange crystalline material. Yield: 0.16 g, 71% (Found: C, 67.0; H, 7.51; N, 1.5; S, 3.5. Calc. for $C_{48}H_{62}BNP_2RuS$: C, 67.1; H, 7.28; N, 1.6; S, 3.7%). IR: ν(C=C) 1563 cm^{-1}. NMR [$(CD_3)_2$-CO]: ^1H, δ 5.10 (s, C_5H_5), 12.25 (s, br, NH), 8.18 (d, J 8), 7.74 (d, J 8), 7.62 (t, J 7) and 7.03 (t, J 7 Hz); ^{31}P-{^1H}, δ 88.4 (s).

[RuCp(SC$_6$H$_3$N$_2$)(dippe)][BPh$_4$] 12. A procedure analogous to that for complex **10** was followed starting from [RuCpCl-(dippe)] (0.13 g, 0.28 mmol) and pyrimidine-2-thiol (HSPym, 0.04 g). The product was obtained as an orange crystalline material. Yield: 0.18 g, 76% (Found: C, 65.7; H, 7.03; N, 2.9; S, 3.5. Calc. for $C_{47}H_{61}BN_2P_2RuS$: C, 65.7; H, 7.10; N, 3.3; S, 3.7%). IR: ν(C=C) 1603, 1548; ν(NH) 3259 cm^{-1}. NMR [$(CD_3)_2CO$]: ^1H, δ (298 K) 5.07 (s br, C_5H_5), 13.28 (s, br, NH) and 8.48 (br, C); (203 K) 5.04 (s br, C_5H_5), 13.66 (s, br, NH), 8.77, 8.08 and 7.11 (br, C); ^{31}P-{^1H}, δ (298 K) 90.1 (s br, $\Delta\nu_{1/2} \approx 140$); (203 K) 89.1 (s br, $\delta\nu_{1/2} \approx 54$ Hz).

Crystal structure determinations

Details are given in Table 1. Data collection was carried out using an AFC6S-Rigaku automatic diffractometer in the $\omega/2\theta$ scan mode with monochromated Cu-Kα radiation for compound [RuCp(SPh)(dippe)][BPh$_4$] and Mo-Kα radiation for [RuCp(SPh)(dippe)]. The structures were solved by Patterson methods and subsequent expansion of the models using DIRDIF.[18] Reflections having $I > 3\sigma(I)$ were used for structure refinement. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included at idealized positions and not refined. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[19] software system and ORTEP[20] for plotting. Maximum and minimum peaks in the final Fourier-difference maps were +1.76 and −1.45 e Å^{-3} for **6**, and +0.56 and −0.64 e Å^{-3} for **9**.

CCDC reference number 186/1714.

See http://www.rsc.org/suppdata/dt/1999/4309/ for crystallographic files in .cif format.

Results and discussion

The complexes [RuCp*Cl(dippe)] reacts with H_2S and $NaBPh_4$ in MeOH furnishing the ruthenium(IV) hydridothiol [RuCp*-H(SH)(dippe)][BPh$_4$] **1**, which was isolated as a microcrystalline material in *ca.* 60% yield, and it represents just the second account of the formation of such oxidative addition type species. The preparation of this compound follows our recent report of the related hydridometallothiol complex [RuCp*-H(SH)(PEt$_3$)$_2$][BPh$_4$], which was structurally characterized by X-ray crystallography and showed a transoid four-legged piano-stool geometry for the complex cation.[13] An analogous structure can be proposed for compound **1** based upon NMR spectral data. Triplet resonances for the hydrido and mercapto protons are observed in the ^1H NMR spectrum at δ −9.42 ($^2J_{HP}$ = 35.8) and −2.35 ($^3J_{HP}$ = 7 Hz) respectively, whereas the ^{31}P-{^1H} NMR spectrum consists of one singlet at δ 70.9. The presence of the Cp* ligand determines the occurrence of the oxidative addition product, since the reaction of [RuCpCl-(dippe)] with H_2S under the same conditions yielded only the green binuclear disulfido complex [{RuCp(dippe)}$_2$(μ-S$_2$)]-[BPh$_4$]$_2$ **2**. The analogous Cp* species [{RuCp*(dippe)}$_2$(μ-S$_2$)]-[BPh$_4$]$_2$ **3** can be obtained by exposing solutions of **1** to air. Both **2** and **3** are also accesible in good yields by reaction of either [RuCp*Cl(dippe)] or [RuCpCl(dippe)] with the stoichiometric amount of S_8 and $NaBPh_4$ in MeOH, as in case of the derivatives [{Ru(C$_5$R$_5$)(PR′$_3$)$_2$}$_2$(μ-S$_2$)$_2$][BPh$_4$]$_2$ (R = H, PR′$_3$ = PPh_3 or PMe_3; R = H or Me, PR′$_3$ = PEt_3).[13,21] These disulfide derivatives are characterized by the presence of a strong charge-transfer band around 800 nm, which is responsible for their intense green colour. Their binuclear nature was confirmed by the presence of peaks in the FAB-MS corresponding to the parent ion at m/z 921 and 1062 respectively for **2** and **3**. Hence, the reactivity of [RuCp*Cl(dippe)] and [RuCpCl-(dippe)] towards H_2S parallels that of their PEt_3 counterparts. However when we attempted to carry out reactions of [RuCp*-Cl(PEt$_3$)$_2$] and [RuCpCl(PEt$_3$)$_2$] with organic thiols complex mixtures were obtained from which no pure compounds were isolated. At variance with this, [RuCp*Cl(dippe)] reacted cleanly with HSPh in MeOH in the presence of $NaBPh_4$ affording the purple ruthenium(III) thiolate complex [RuCp*(SPh)-(dippe)][BPh$_4$] **4**, even under an inert atmosphere of N_2 or Ar. Yields are improved by working in the air. Complex **4** is paramagnetic, having an effective magnetic moment in solution of 2.4 μ_B at 295 K, consistent with the presence of one unpaired electron in the complex cation. All efforts to isolate the thiol adduct [RuCp*(HSPh)(dippe)][BPh$_4$] by rigorous oxygen exclusion from the reaction mixture proved to be unsuccessful. However it was possible to isolate the benzenethiol complex [RuCp(HSPh)(dippe)][BPh$_4$] **5** as an extremely air-sensitive golden brown microcrystalline material. This diamagnetic compound displays one weak band at 2483 cm^{-1} in its IR spectrum ascribed to ν(SH) in co-ordinated PhSH. The sulfur-bound proton appears as one broad resonance at δ 2.90 in the ^1H NMR spectrum, in the range previously observed for other thiol complexes of ruthenium.[3–6] No spectral evidence supporting the occurrence of an isomerization process or equilibrium with the hydrido(benzenethiolate) tautomer [RuCpH(SPh)-(dippe)][BPh$_4$] has been obtained.

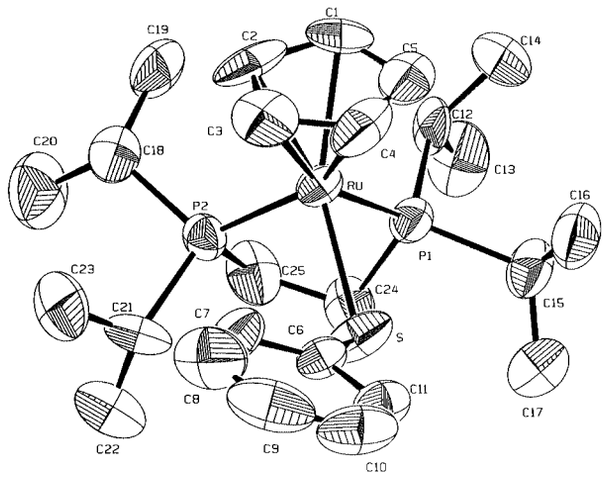


Fig. 1 An ORTEP view of the complex cation [RuCp(SPh)(dippe)]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted.

Air oxidation of complex **5** led to the ruthenium(III) thiolate [RuCp(SPh)(dippe)][BPh$_4$] **6** in quantitative yield. As in the case of compound **4**, **6** contains also one unpaired electron as indicated by the value of its effective magnetic moment of 2.1 μ_B at 301 K. The crystal structure of **6** was determined. An ORTEP view of the complex cation is shown in Fig. 1. Relevant bond distances and angles are listed in Table 2. The structure consists of a packing of [BPh$_4$]$^-$ anions and [RuCp(SPh)(dippe)]$^+$ cations. The cation exhibits a pseudo-octahedral three-legged piano-stool structure, in which three co-ordination positions are occupied by the cyclopentadienyl ligand. The Ru(1)–S(1) separation of 2.272(2) Å is short, and compares well with the value found in the ruthenium(III) thiolate complex [RuCp-(SBu^t)(PPh$_2$(OMe))$_2$][PF$_6$] (2.274(1) Å),[3b] being indicative of a strong metal–sulfur interaction. A similar short Ru–S separation (2.303(3) Å) was also found in the five-co-ordinate complex [Ru(SPh)(dippe)$_2$][BPh$_4$],[8] and explained in terms of a significant Ru–S π bonding. In this particular case this interaction increases the electron count at the ruthenium atom, so the complex is not strictly a 16-electron co-ordinatively

Table 1 Summary of data for the crystal structure analysis of complexes **6** and **9**

	6	**9**
Formula	$C_{49}H_{62}BP_2RuS$	$C_{25}H_{42}P_2RuS$
M	856.92	537.68
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	*Pbac* (no. 61)
a/Å	13.277(4)	19.449(4)
b/Å	13.610(3)	17.442(2)
c/Å	13.053(3)	15.578(2)
α/°	96.97(2)	
β/°	103.869(10)	
γ/°	101.16(2)	
V/Å^3	2211(2)	5284(2)
Z	2	8
μ/cm^{-1}	42.9 (Cu-Kα)	7.86 (Mo-Kα)
T/K	290	290
Unique reflections	6885	3891
Observed reflections ($I > 3\sigma_I$)	4046	1658
R	0.058	0.050
R′ ($w = \sigma_F^{-2}$)	0.074	0.062

Table 2 Selected bond distances (Å) and angles (°) for [RuCp(SPh)(dippe)][BPh_4]

Ru(1)–S(1)	2.272(2)	Ru(1)–C(3)	2.249(7)
Ru(1)–P(1)	2.339(2)	Ru(1)–C(4)	2.234(9)
Ru(1)–P(2)	2.324(2)	Ru(1)–C(5)	2.273(8)
Ru(1)–C(1)	2.254(8)	S(1)–C(6)	1.781(8)
Ru(1)–C(2)	2.246(7)		
S(1)–Ru(1)–P(1)	93.99(8)	S(1)–Ru(1)–C(4)	97.0(3)
S(1)–Ru(1)–P(2)	84.92(7)	S(1)–Ru(1)–C(5)	110.0(3)
S(1)–Ru(1)–C(1)	144.9(3)	P(1)–Ru(1)–P(2)	82.31(7)
S(1)–Ru(1)–C(2)	153.9(2)	Ru(1)–S(1)–C(6)	113.1(3)
S(1)–Ru(1)–C(3)	117.2(2)		

unsaturated species. In the case of **6**, which is formally a 17-electron system, π donation of electron density from sulfur to ruthenium has the same compensating effect, resulting in a Ru–S bond length consistent with a bond order of 1.5.[22] 17-Electron complexes of the type $[RuCp(SPh)(L)_2]^+$ (L = 1/2 dppe, PMe_3, $P(OMe)_3$ or $PPh_2(OMe)$) have been prepared by oxidation of thiol or neutral thiolate complexes using Ag^+ or air as oxidant.[3] It appears that good donor phosphine ligands help to stabilize the Ru^{III}. In other cases where phosphines are not present, oxidation may happen at the sulfur atom, leading to dimerization, *i.e.* $[\{RuCp(CO)_2\}_2(\mu\text{-}Ph_2S_2)]^{2+}$,[3a] a process which is apparently related to formation of the disulfide species $[\{RuCp(L)_2\}_2(\mu\text{-}S_2)]^{2+}$ either from $[RuCp(SH_2)(L)_2]^+$ *via* $[RuCp(SH)(L)_2]$,[21] or from $[RuCp^*H(SH)(L)_2]^+$.[13] This suggests that the final oxidation product not only depends on the presence of phosphines acting as co-ligands, but also on the nature of the sulfur donor. We proposed recently the oxidation of the putative mercapto complex $[RuCp^*(SH)(PEt_3)_2]$ to explain the formation of $[\{RuCp^*(PEt_3)_2\}_2(\mu\text{-}S_2)]^{2+}$ at the expense of the hydridometallothiol $[RuCp^*H(SH)(PEt_3)_2]^+$. However, we failed in isolating or detecting the neutral intermediate mercapto complex, which should be generated by proton dissociation from $[RuCp^*H(SH)(PEt_3)_2]^+$.[13] We have now been able to isolate [RuCp*(SH)(dippe)] **7** as an orange crystalline material, by deprotonation of **1** using the stoichiometric amount of LDA as proton acceptor. Compound **7** is characterized by the presence of one medium *ν*(SH) band at 2540 cm^{-1}, and one triplet resonance at *δ* −3.95 ($^3J_{HP} = 6$ Hz) in its ^1H NMR spectrum attributable to the mercapto proton. Its ^{31}P-$\{^1H\}$ NMR spectrum consists of one sharp singlet, suggesting a three-legged piano-stool structure, as has been proposed for the related derivative $[RuCp(SH)(PPh_3)_2]$.[12] Protonation of **7** at low temperature in acetone failed to yield the hydrogen sulfide adduct $[RuCp^*(SH_2)(dippe)]^+$, and instead the hydridometallothiol derivative **1** was the only product identified by NMR spectroscopy, being isolated thereafter in essentially quantitative yield. This observation demonstrates the reversibility of the deprotonation/protonation processes involving compounds **1** and **7**. Compound **7** is readily oxidized by atmospheric oxygen in solution, as inferred from the colour change to deep green. This colour suggests the formation of species containing the disulfido unit μ-S_2, although different products are formed depending on the solvent. Thus, exposure of acetone or dichloromethane solutions of **7** to air resulted in the formation of $[\{RuCp^*(dippe)\}_2(\mu\text{-}S_2)]^{2+}$ as shown by NMR spectroscopy. However, when the oxidation was performed in benzene a green solution displaying one sharp singlet at *δ* 84.1 in its ^{31}P-$\{^1H\}$ NMR spectrum was obtained. We have tentatively assigned this resonance to the neutral binuclear disulfide complex $[\{RuCp^*(dippe)\}_2(\mu\text{-}S_2)]$, but have been unable to isolate it as a solid in pure form. The chemical and electrochemical oxidation reactions of $[RuCp(SH)(PPh_3)_2]$ have been studied in detail,[12] and shown to be complex processes which lead to species containing the μ-S_2 core, consistent with our observations. The isolation of **7** from the hydrido(metallothiol) **1**, and its oxidation to $[\{RuCp^*(dippe)\}_2(\mu\text{-}S_2)]^{2+}$, is in strong support of our tentative reaction sequence previously proposed to explain the formation of the binuclear disulfide complex $[\{RuCp^*(PEt_3)_2\}_2(\mu\text{-}S_2)]^{2+}$ at the expense of $[RuCp^*H(SH)(PEt_3)_2]^+$. Scheme 1 summarizes the reactivity of [RuCp*Cl(dippe)] towards H_2S and HSPh, for comparison purposes.

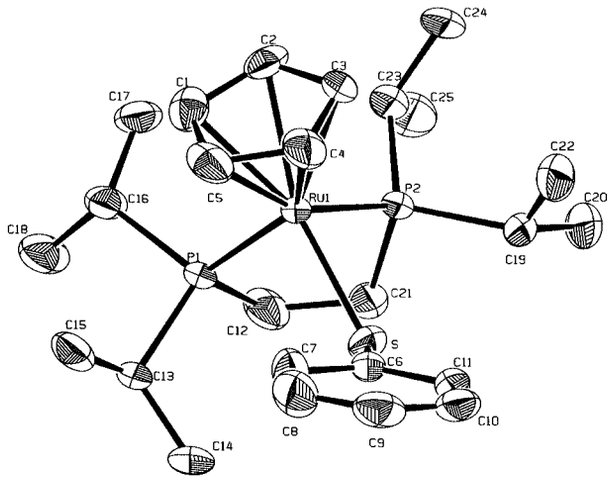
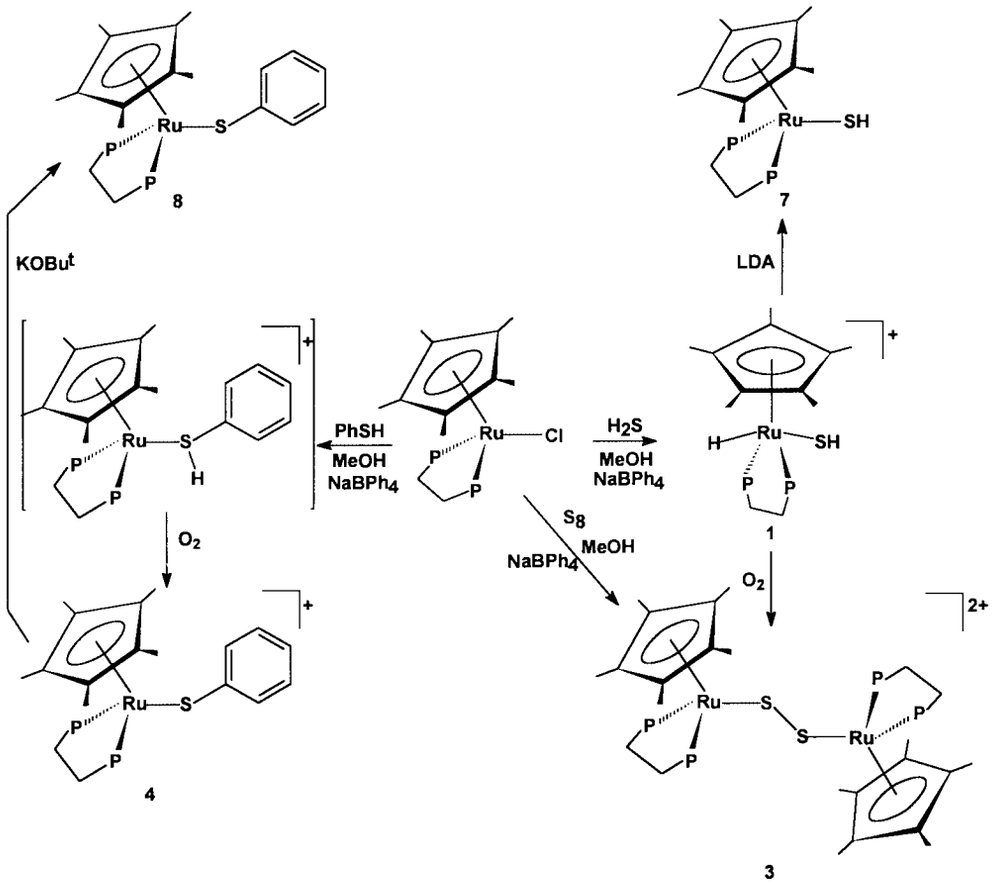


Fig. 2 An ORTEP view of the complex [RuCp(SPh)(dippe)]. Details as in Fig. 1.

Treatment of the ruthenium(III) complex **4** with $KOBu^t$ yielded the neutral diamagnetic benzenethiolate derivative [RuCp*(SPh)(dippe)] **8**. Likewise, [RuCp(SPh)(dippe)] **9** was obtained by reaction of either **5** or **6** with $KOBu^t$ in tetrahydrofuran. There are recent reports of the easy reduction of ruthenium(III) to ruthenium(II) species by treatment with a Lewis base,[23] whereas the formation of **9** from **5** can be considered a simple deprotonation reaction. Compounds **8** and **9** are orange crystalline materials which exhibit one single resonance in their ^{31}P-$\{^1H\}$ NMR spectra as expected. However, in the case of **9**, this resonance is very broad at room temperature ($\delta\nu_{1/2} = 805$ Hz), at variance with that for **8**, which is very sharp. The resonances in the ^1H NMR spectrum of **9** are also broad. These resonances sharpen when the temperature is lowered, indicating that the dynamic process responsible for this behaviour becomes slower. Such a process is most likely the inversion of the electron pair at the sulfur atom, causing a "spanning" movement of the R group attached to sulfur, as it has been observed in other instances.[24] The barrier for this dynamic process is higher in the case of the pentamethylcyclopentadienyl derivative **8** due to the steric hindrance, which increases the



Scheme 1 Compared reactivity of [RuCp*Cl(dippe)] towards HSPh and H_2S.

Table 3 Selected bond distances (Å) and angles (°) for [RuCp(SPh)(dippe)]

Ru(1)–S(1)	2.420(4)	Ru(1)–C(3)	2.22(1)
Ru(1)–P(1)	2.304(4)	Ru(1)–C(4)	2.21(2)
Ru(1)–P(2)	2.289(4)	Ru(1)–C(5)	2.25(1)
Ru(1)–C(1)	2.23(1)	S(1)–C(6)	1.76(1)
Ru(1)–C(2)	2.18(1)		
S(1)–Ru(1)–P(1)	84.6(1)	S(1)–Ru(1)–C(4)	91.0(5)
S(1)–Ru(1)–P(2)	93.0(1)	S(1)–Ru(1)–C(5)	112.2(5)
S(1)–Ru(1)–C(1)	148.8(5)	P(1)–Ru(1)–P(2)	83.2(1)
S(1)–Ru(1)–C(2)	140.7(6)	Ru(1)–S(1)–C(6)	112.6(4)
S(1)–Ru(1)–C(3)	103.8(5)		

rigidity of the system. The molecular structure of **9** was elucidated by crystal structure analysis. An ORTEP view of the molecule is shown in Fig. 2. Relevant bond lengths and angles are listed in Table 3. The structure consists of a packing of neutral molecules separated by van der Waals contacts. Each of these molecules shows the expected three-legged piano-stool geometry with an arrangement of the benzenethiolate ligand very similar to that adopted by the complex cation [RuCp(SPh)(dippe)]$^+$ in compound **6** (Fig. 1). The main difference between these two structures lies in the value of the Ru(1)–S(1) bond length of 2.420(4) Å for **9**, which is significantly longer than in **6**, but fully consistent with values reported for other ruthenium(II) thiolate complexes, usually in the range 2.40–2.43 Å.[9] It is interesting that the neutral thiolates **8** and **9** are quite stable towards oxidation by atmospheric oxygen, both in the solid state and in toluene or diethyl ether solution. In contrast with this, acetone, dichloromethane or alcoholic solutions became purple immediately in contact with the air, indicating rapid oxidation to ruthenium(III).

As we did with the PEt_3 system, we have also examined the reactivity of [RuCp*Cl(dippe)] and [RuCpCl(dippe)] towards pyridine-2-thiol HSPy, and in analogous fashion the complexes [RuCp*(S=CCH=CHCH=CHNH)(dippe)][BPh_4] **10** and [RuCp(S=CCH=CHCH=CHNH)(dippe)][BPh_4] **11** were obtained. The related derivative [RuCp(S=CN=CHCH=CHNH)(dippe)][BPh_4] **12** was also prepared by reaction of [RuCpCl(dippe)] with pyrimidine-2-thiol (HSPym) and $NaBPh_4$, although we failed in obtaining its Cp* counterpart. As we had previously noted for the PEt_3 derivatives, compounds **10**–**12** are characterized by the presence of one broad resonance in the range δ 10–12 attributable to nitrogen-bound protons, suggesting that also in this case both HSPy and HSPym exist in their complexes respectively as S-bound 1*H*-pyridine-2-thione or 1*H*-pyrimidine-2-thione tautomers. Such tautomeric processes are well established.[25] In the case of compound **12** the broadness of the resonances in its NMR spectra has been interpreted in terms of an additional tautomeric equilibrium involving rapid proton exchange between the two nitrogen atoms present in the ligand. At variance with other complexes described in this work, **10**–**12** are air stable both in the solid state and in solution. In this sense it can be concluded that the co-ordination chemistry of HSPy and HSPym appears quite different to that of other organic thiols, being not representative.

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